

NATIONAL BUREAU OF STANDARDS REPORT

5430

REPORT ON DENTAL RESEARCH
AT THE NATIONAL BUREAU OF STANDARDS

Progress Report

January 1 to June 30, 1957

Dental Research Laboratory



**U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS**

THE NATIONAL BUREAU OF STANDARDS

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The functions of the National Bureau of Standards are set forth in the Act of Congress, March 3, 1901, as amended by Congress in Public Law 619, 1950. These include the development and maintenance of the national standards of measurement and the provision of means and methods for making measurements consistent with these standards; the determination of physical constants and properties of materials; the development of methods and instruments for testing materials, devices, and structures; advisory services to Government Agencies on scientific and technical problems; invention and development of devices to serve special needs of the Government; and the development of standard practices, codes, and specifications. The work includes basic and applied research, development, engineering, instrumentation, testing, evaluation, calibration services, and various consultation and information services. A major portion of the Bureau's work is performed for other Government Agencies, particularly the Department of Defense and the Atomic Energy Commission. The scope of activities is suggested by the listing of divisions and sections on the inside of the back cover.

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Information on the Bureau's publications can be found in NBS Circular 460, Publications of the National Bureau of Standards (\$1.25) and its Supplement (\$0.75), available from the Superintendent of Documents, Government Printing Office, Washington 25, D. C.

Inquiries regarding the Bureau's reports should be addressed to the Office of Technical Information, National Bureau of Standards, Washington 25, D. C.

NATIONAL BUREAU OF STANDARDS REPORT

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5430

REPORT ON DENTAL RESEARCH AT THE NATIONAL BUREAU OF STANDARDS

Progress Report

January 1 to June 30, 1957

Dental Research Laboratory

The dental research program at the National Bureau of Standards is carried on in cooperation with the Council on Dental Research of the American Dental Association, the Army Dental Corps, the Air Force Dental Service, the Navy Dental Corps, and the Veterans Administration.

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U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

REPORT ON DENTAL RESEARCH
AT THE NATIONAL BUREAU OF STANDARDS

1. INTRODUCTION

Research on a wide range of dental restorative materials and equipment and on natural tooth structures has continued at the National Bureau of Standards during the half year ending June 30, 1957.

Summaries of results obtained on work in progress, a list of reports issued on completed phases of several projects and a list of papers published during the period are given below. Copies of the reports are appended.

2. REPORTS ISSUED

- NBS Report 5209 The Reaction of Zinc Oxide with o-Ethoxybenzoic Acid and other Chelating Agents.
NBS Report 5340 Physical Properties of Chromium-Cobalt Dental Alloys.
NBS Report 5348 Colors of Dental Silicate Cements.
NBS Report 5397 Mechanical Mixing of Dental Cements.

3. PAPERS PUBLISHED

A Panoramic Dental X-ray Machine. D. C. Hudson, J. W. Kumpula and George Dickson. Armed Forces Med. J. 8:46 Jan. 1957.

A Method for Measuring the Mucosal Surface Contours of Impressions, Casts and Dentures. N. W. Rupp, George Dickson, M. E. Lawson, Jr., and W. T. Sweeney. JADA 54:24 Jan. 1957.

A Proposed Specification for Dental Chromium-Cobalt Casting Alloys. Duane F. Taylor and W. T. Sweeney. JADA 54:44 Jan. 1957.

A Simple Technic for Making Dental Porcelain Jacket Crowns. Hector Sacchi and George C. Paffenbarger. JADA 54:366 Mar. 1957.

Alginate Impression Materials. H. J. Caul. JADA 54:567 April 1957.

Methods for Evaluation of Rotating Diamond-Abrasive Dental Instruments. J. L. Hartley, D. C. Hudson, W. T. Sweeney and George Dickson. JADA 54:637 May 1957.

Apatites Deficient in Divalent Cations. A. S. Posner and A. Perloff. J. Research NBS 58:279 May 1957.

Proposed Specification for Plastic Teeth. W. T. Sweeney, R. L. Myerson, E. E. Rose and J. O. Semmelman. J. Pros. Dent. 7:420 May 1957.

Changes in Agar-Agar Duplicating Material and Agar-Agar on Heating and Storage. Peter M. Margetis and W. C. Hansen JADA 54: 737 June 1957.

4. WORK IN PROGRESS

4.1 Human Tooth Enamel and Dentin

(a) Fluorescence Studies.

Investigation of the feasibility of carrying on interference microscopy studies in conjunction with the work on fluorescence of tooth structures was continued. It was found that the tooth sections used for fluorophotomicroscopy were too thick for proper observation of the interference band displacement. Work is now in progress to prepare ultra thin sections.

In response to many requests from research investigators and manufacturers for phosphor reference samples which could be used to calibrate fluorescence and phosphorescence detectors and as standards in the manufacture of fluorescent and phosphorescent articles, sets of fourteen reference phosphors are being prepared. The phosphors were made available through the cooperation of the Electrochemical Society, the Naval Research Laboratory, the National Bureau of Standards, and the American Dental Association. At present these samples will serve as arbitrary reference standards only. A project on the fundamental properties of these phosphors may be undertaken later.

(b) Crystallographic Studies.

Calculations of the least squares analysis of the single crystal x-ray diffraction data on calcium apatite $[Ca_{10}(PO_4)_6(OH)_2]$ by means of the IBM 704 (electronic computer) were completed. Improved atomic parameters have been delineated from this work. The x-ray single crystal data on lead apatite $[Pb_{10}(PO_4)_6(OH)_2]$ were obtained and were prepared for machine calculations of the atomic parameters.

A low angle diffraction camera for use in studies of particle size distribution in tooth and osseous tissue was designed and construction started.

Infrared absorption studies in cooperation with E. R. Lippencott, Dept. of Chemistry, University of Maryland, have indicated that hydrogen bonding is present in bone and tooth mineral as well as in synthetic defect apatites. Pure apatite

crystals gave no sign of hydrogen bonding. Treatment of defect apatites with calcium acetate which reduced the solubility and increased the Ca/P ratio also reduced the intensity of hydrogen bonding absorption bands.

4.2 Metals

(a) Amalgam.

Ag-Sn-Hg System Studies.

Effort has been devoted to a revision of methods of investigation of the Ag-Sn-Hg system. Construction of vapor pressure apparatus for the study of the equilibrium vapor pressures of the various phases, is nearing completion. Room temperature x-ray diffraction tests raised a question as to whether the accepted solubility limits in the Sn-Hg system are in error or whether the samples contain free Hg. Specimens and low temperature adaptors for x-ray diffraction studies below the freezing point of mercury are being prepared.

Amalgam Setting Time.

In the course of evaluating the precision and accuracy of the setting time test for amalgam, it has been observed that the carving time of the alloys under study is effected by storage environment and tenure. It has been found that the carving time of most commercial amalgam alloy preparations increases with time of storage at room temperature in a linear fashion. Acceleration of room temperature storage effects may be achieved at 212°F, and tests on alloys stored at this temperature for four hours indicate that alloy storage at room temperature would have a continued effect on carving time for a number of years. Further work on this project will be done to (1) further evaluate the importance of the operator variable, (2) utilize the test to develop specification requirements, and (3) utilize the test to develop a better understanding of the mechanism which causes the changes in the carving time of dental amalgam.

(b) Gold Foil.

The availability of a crosshead-type testing unit of unusually high accuracy has permitted the study of moderately low strength materials such as condensed gold foil in which specimen sizes more nearly approximating the dental application may be used.

Specimens, 2 mm in thickness, have received preliminary study for the gold foil and amalgam materials. Preliminary tests using amalgam specimens have provided reproducible data. Before further work is undertaken, however, a correlation will be obtained between the strain data (as indicated by the crosshead travel) recorded by the testing unit, and strain data obtained from SR-4 type A-18 gauges located directly on the gauge length of the amalgam specimen. Since dental amalgam is a particularly brittle material, the comparative information thus obtained should enable corrections in strain measurement error permitting a high order of accuracy in the strain values obtained for gold foil. A committee of the American Academy of Gold Foil Operators has been set up to assist in producing suitable specimens in shapes such that better physical constants can be obtained on this type of restorative material.

4.3 Resins

(a) Denture Reliners.

Partially completed analyses have provided additional information on the composition of denture reliners sold directly to the public. Principal components which differ widely from brand to brand, include the following poly [vinyl acetate], poly [n-butyl methacrylate], paraffin, triacetin, and natural gums such as tragacanth and karaya. Apparently many other constituents are present including coloring and flavoring materials, water and calcium, magnesium and potassium salts.

A systematic study of the properties of denture reliners used by the dental profession has been initiated. Such properties as porosity, heat rise on curing, water solubility and sorption and effect on transverse strength of denture base materials are being determined.

(b) Denture Base Resins.

A study of the physical properties and clinical characteristics of different types of denture base resins including heat curing and self curing poly [methyl methacrylate] with and without cross-linkage, vinyl-acrylic resin copolymers and poly styrene - rubber copolymers has been initiated.

(c) Silica-Resin Direct Filling Material.

Additional batches of products of epoxy acrylate esters were synthesized and physical properties obtained. Another synthesis was made using bisphenol A and glycidyl methacrylate. Viscosity was reduced with tetraethylene glycol dimethacrylate.

When activated with approximately 1% dimethyl para toluidene and mixed with clear fused quartz powder containing 1% benzoyl peroxide this material hardened at room temperature in about $1\frac{1}{2}$ minutes. The material exhibits good qualitative properties of hardness and visual matching of tooth structure.

(d) Polymerization Reactions.

The studies of the rate of free radical formation of the peroxide-amine initiator-accelerator system in air were completed. The kinetics of this reaction is complex. Measurement of the kinetics in a vacuum is now under active investigation. The rate of the apparent free radical formation is greatly slowed down by the presence of air and difficulties were encountered in removing traces of air. New experimental techniques are being developed to eliminate the presence of minute quantities of air which greatly affect the measurements.

(e) Gas Chromatography.

Copolymers of methyl methacrylate with varying percentage of acrylic and methacrylic esters as well as acrylic and methacrylic acid were synthesized. Liquid pyrolysis products obtained on heating the specimen to 350°C were analyzed by gas chromatographic procedures using a dinonyl phthalate-firebrick column. Other columns were also prepared and their usefulness in polymer identification being studied. A series of cross linked methyl methacrylate copolymers were obtained and the effect of cross linking agents on the chromatograms is being studied.

4.4 Elastic Impression Materials

(a) Alginate Materials.

The physical properties of a large number of commercial dental alginate impression materials have been studied. New tests for consistency, working time, detail reproduction, and deterioration have been devised and included in a complete revision of the Federal Specification for these materials. A draft of this proposed revision is being prepared for distribution to cooperating agencies for their comments.

(b) Synthetic Rubber Base Materials.

Additional data were obtained on the properties including setting time, working time, strain, permanent deformation, flow, dimensional stability, compatibility with gypsum, and detail reproduction of thiokol and silicone impression materials. On

the basis of these data a tentative proposed specification for synthetic rubber base impression materials has been written.

4.5 Color Standards

A progress report on the colors of silicate cements is appended. Data are being obtained on the effects of blending shades of different colors, on the effects of aging the cements at temperatures above room temperatures and on the limits of precision of determinations of the cement colors with the Gardner Color Difference Meter.

4.6 Zinc Oxide Materials

The reaction of zinc oxide with chelating agents was continued. Chelating agents containing phenolic, enolic or carboxylic acid groups react with zinc oxide to form hard coherent products. Many of these materials disintegrate slowly in water. The solubility of hardened mixes containing o-ethoxybenzoic acid-eugenol, zinc oxide and quartz can be decreased somewhat by incorporation into the mix of 3 to 5% of a silicone.

Chelators containing acid groups act as accelerators in the hardening of zinc oxide-eugenol mixtures.

4.7 Rotating Cutting Instruments

The apparatus for determining the torque-speed characteristics of dental-handpieces was constructed and initial calibration was completed. The instrument permits the operation of the handpieces at several speeds and the simultaneous measurement of (1) delivered torque, (2) bur speed (rpm), (3) motor speed, (4) power input. From these values it is possible to determine the torque-speed curve, the effect of belt slip, and the overall power efficiency of the handpiece-engine combination.

The rotational speeds are measured with photocell-frequency meter pairs and the available torque is measured by a pendulum-optical lever arrangement. Data obtained with the instrument will be used to evaluate the cutting characteristics of tooth structure, using burs and diamond instruments in the overall problem of studying the relationship between fundamental properties of teeth and how best to prepare cavities for dental restorations.

4.8 Dental X-ray Apparatus Survey

Detailed data on the characteristics of dental x-ray apparatus are being obtained from manufacturers. These data will be utilized in answering numerous requests for information on the radiation hazards of x-ray equipment and for advice on methods of eliminating or minimizing such hazards.

4.9 Evaluation of Materials

Materials evaluated for the Federal dental services and the American Dental Association by specification and special test methods included amalgam, denture base resin, inlay casting investment, inlay casting gold alloy, inlay casting wax, mercury, and silicate cement.

For the Director
by



W. T. Sweeney, Chief
Dental Research Section

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Progress Report

THE REACTION OF ZINC OXIDE WITH o -ETHOXYBENZOIC ACID AND OTHER CHELATING AGENTS

by

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This work is a part of the dental research program conducted at the National Bureau of Standards in cooperation with the Council on Dental Research of the American Dental Association, the Army Dental Corps, the Air Force Dental Service, the Navy Dental Corps and the Veterans Administration.

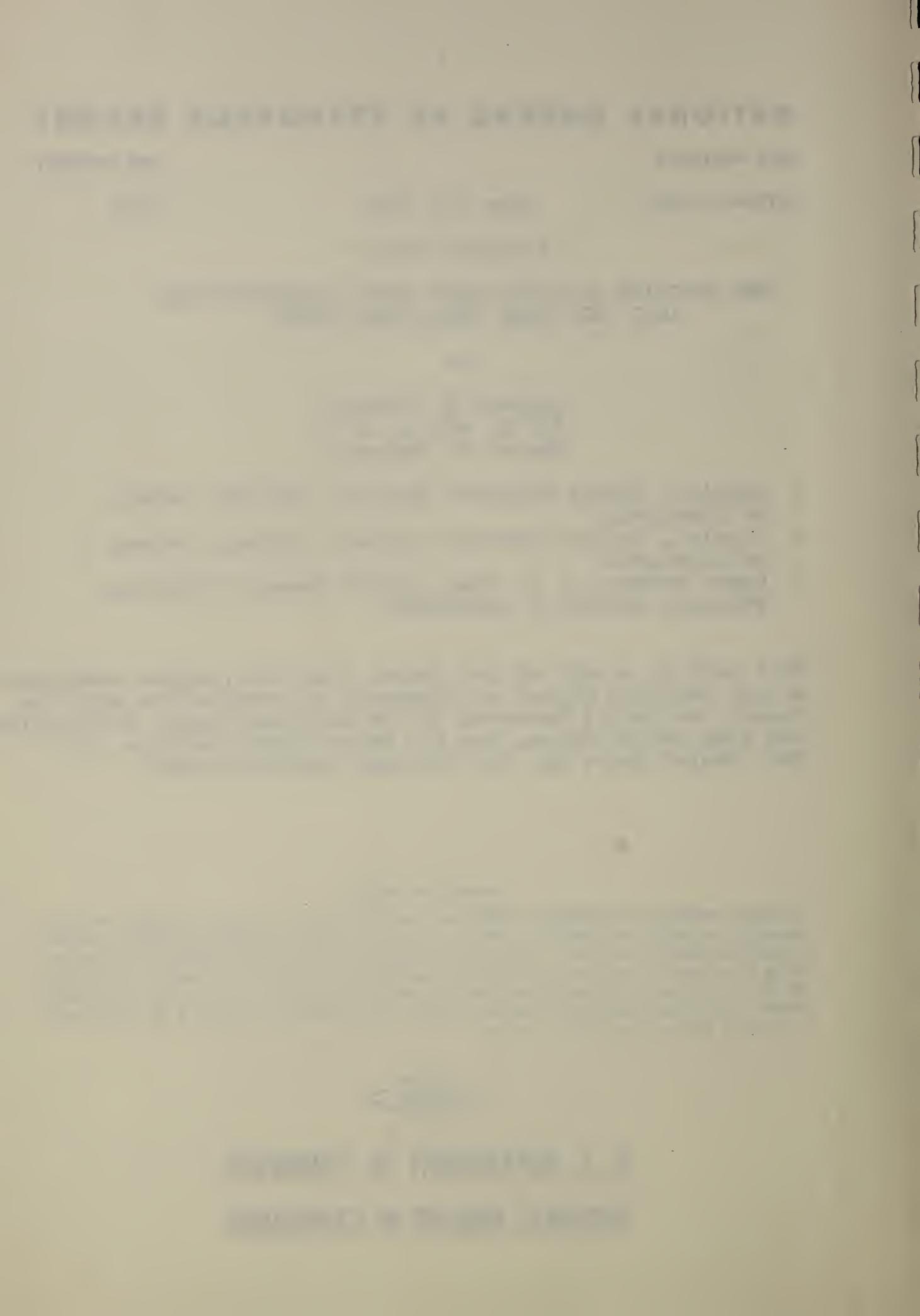
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U. S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS



THE REACTION OF ZINC OXIDE WITH σ -ETHOXYBENZOIC ACID AND OTHER CHELATING AGENTS

Abstract

Zinc oxide-eugenol mixtures have been useful in a number of dental applications. These mixtures form a hard, coherent mass that consists of zinc oxide embedded in a zinc eugenolate chelate matrix. In order to determine the scope of the reaction and to obtain improved products the reaction of metal oxides with organic chelating agents has been investigated.

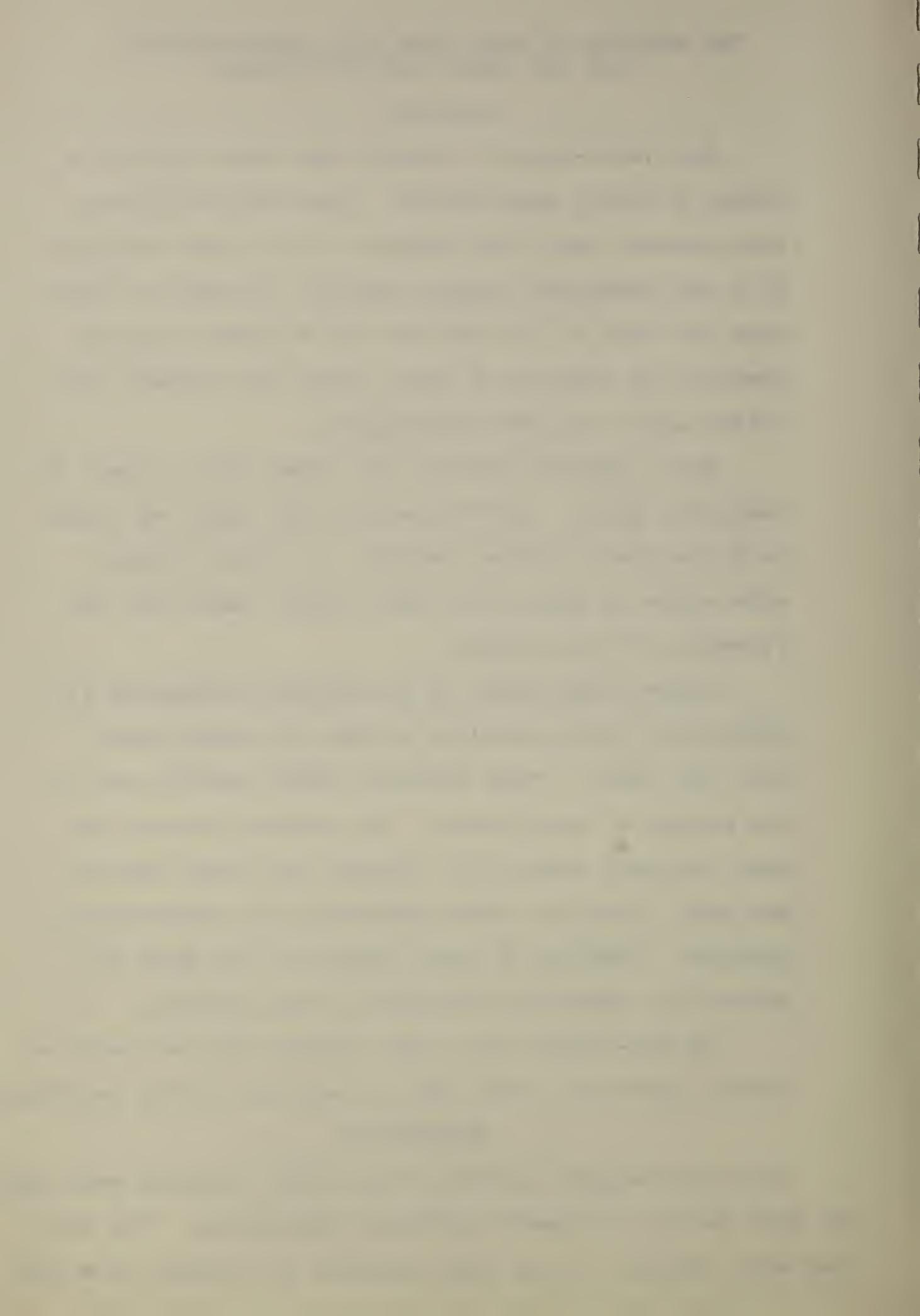
Hard, coherent products are formed with a number of chelating agents. σ -Ethoxybenzoic acid (EBA) was found to be the most suitable chelator. It reacts rapidly with oxides of group II of the periodic table with the formation of hard products.

Further improvement of the physical properties is obtained by using solutions of EBA and eugenol mixed with zinc oxide. These mixtures harden rapidly even in the absence of accelerators. The products formed show much increased compressive strength and higher density and water solubility than commercial zinc oxide-eugenol mixtures. Addition of quartz powder to the mixes improves the compressive strengths of the products.

The EBA-eugenol-zinc oxide mixtures may be useful as dental impression pastes and as temporary filling materials.

1. INTRODUCTION

Zinc oxide-eugenol mixtures form a hard, coherent mass that has been useful in a number of dental applications. The hardened mass consists of zinc oxide embedded in a matrix of a zinc



eugenolate chelate with the empirical formula $(C_{10}H_{11}O_2)_2Zn$ [1]. Mixtures of zinc oxide with ortho substituted phenols such as isoeugenol, guaiacol and methylguaiacol also harden. As would be expected from the reaction mechanism phenols that do not contain ortho substituents or that contain substituents that are incapable of chelation do not undergo this reaction.

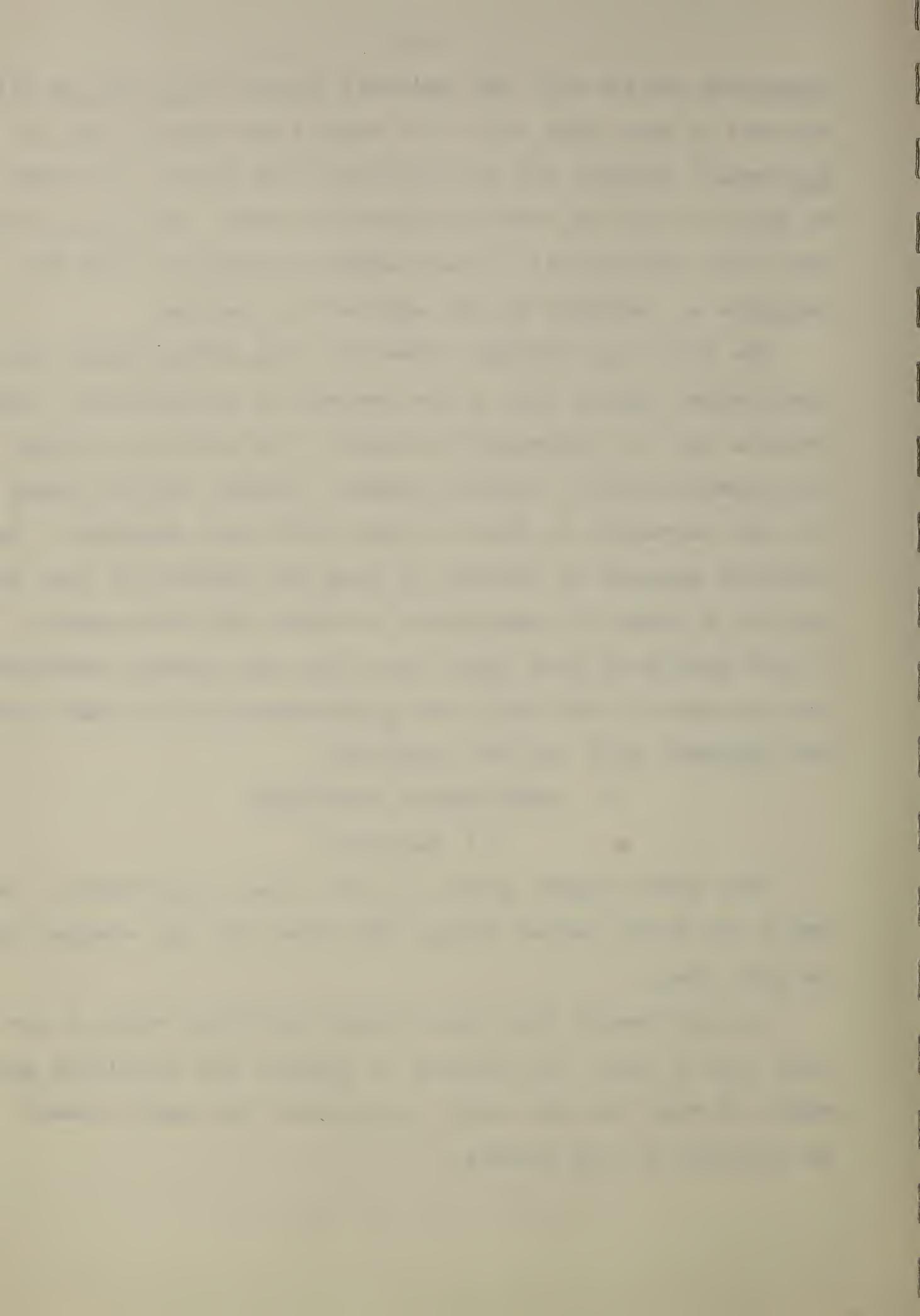
The presently available commercial zinc oxide-eugenol mixtures harden rapidly only in the presence of accelerators. The products have low compressive strength. The materials inhibit the polymerization of acrylic monomers. Hence, acrylic resins will not polymerize in direct contact with these materials. It therefore appeared of interest to study the reaction of zinc oxide with a number of commercially available chelating agents. A large portion of this report deals with the products obtained from mixtures of zinc oxide with o-ethoxybenzoic acid (EBA) since they appeared to be the most promising.

2. EXPERIMENTAL PROCEDURES

2.1 Materials

Zinc oxide reagent grade was used in most experiments. Over 50% of the powder passed through #70 sieve, but was retained by the #100 sieve.

An experimental zinc oxide (Merck Hyperfine) having a particle size of about 0.02 microns in diameter and containing approximately 5% water was also used. Analysis of the sample showed the presence of 1.2% ammonia.



Zinc oxides XX-78, Kadox-72, Kadox-15 and No. 513 were obtained through the courtesy of the New Jersey Zinc Co. Particle size of these materials is given in Table VI. Micronized USP zinc oxide was obtained through the courtesy of the Star Dental Co. Tetrahydroxyethylmethylenediamine was obtained through the courtesy of Visco Products Co., Inc.

Ground, opaque, fused silica (quartz) was procured from the Thermal Syndicate, Ltd. Over 50% of the material passed through the #100 sieve and was retained by the #200 sieve. Silicone R-23 was obtained from the Silicone Division, Union Carbide and Carbon Co.

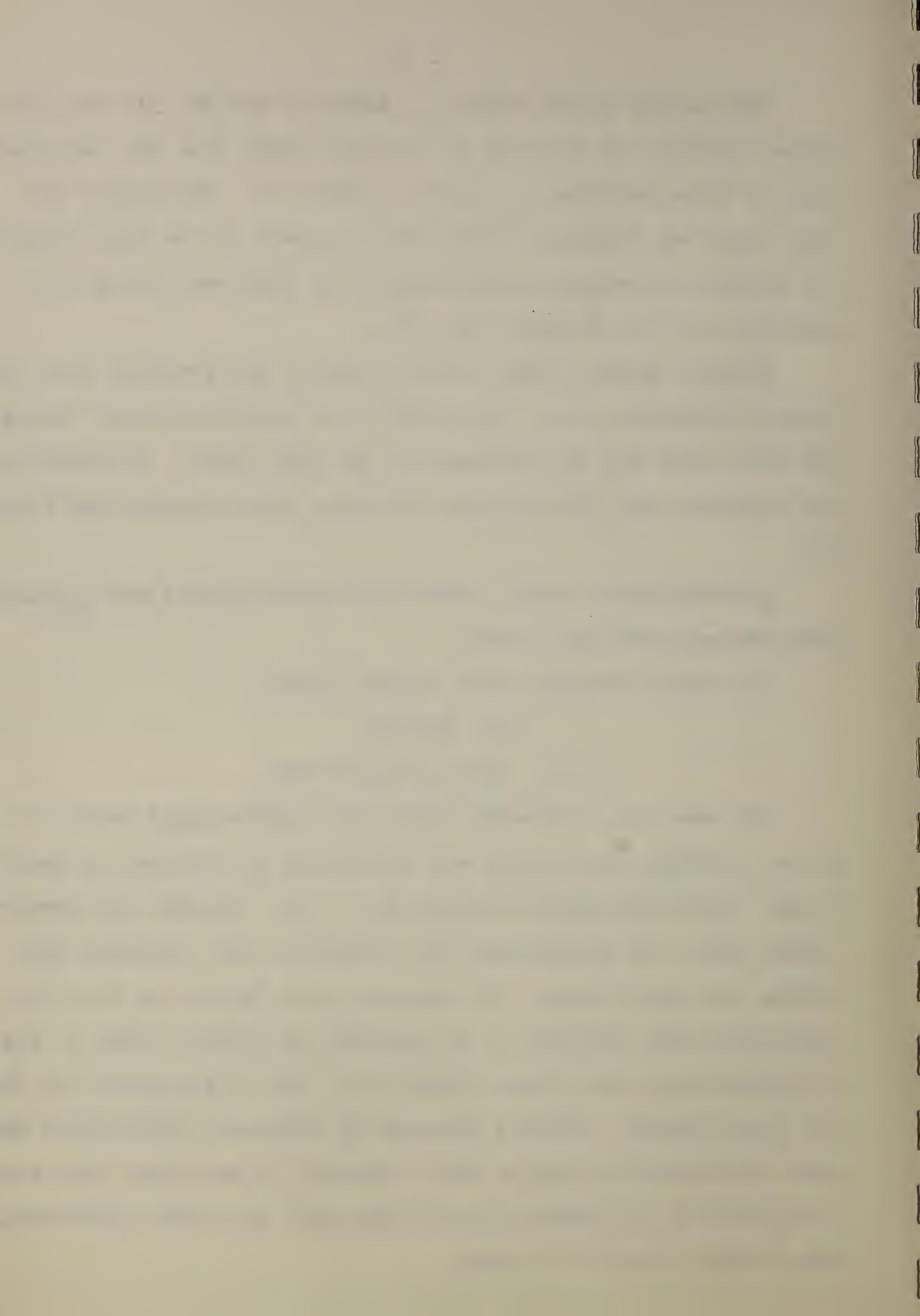
o-Ethoxybenzoic acid, 2-methoxy-4-methylphenol and isoeugenol were Eastman practical grade.

All other chemicals were reagent grade.

2.2 Methods

2.2.1 Consistency of Mix

For some zinc oxide-EBA mixes the powder-liquid ratio of a mix of standard consistency was determined as outlined in American Dental Association Specification No. 9 [2]. Besides the powder-liquid ratio the consistency will depend on the technique used for mixing the constituents. By changing such factors as the rate of spatulation and pressure it is possible to prepare mixes of standard consistency that show variations of 10% in the amount of powder incorporated. Results obtained by different individuals may show variations as high as 10%. However, it was found that such variations of the powder-liquid ratio will not alter appreciably the setting time of the mixes.



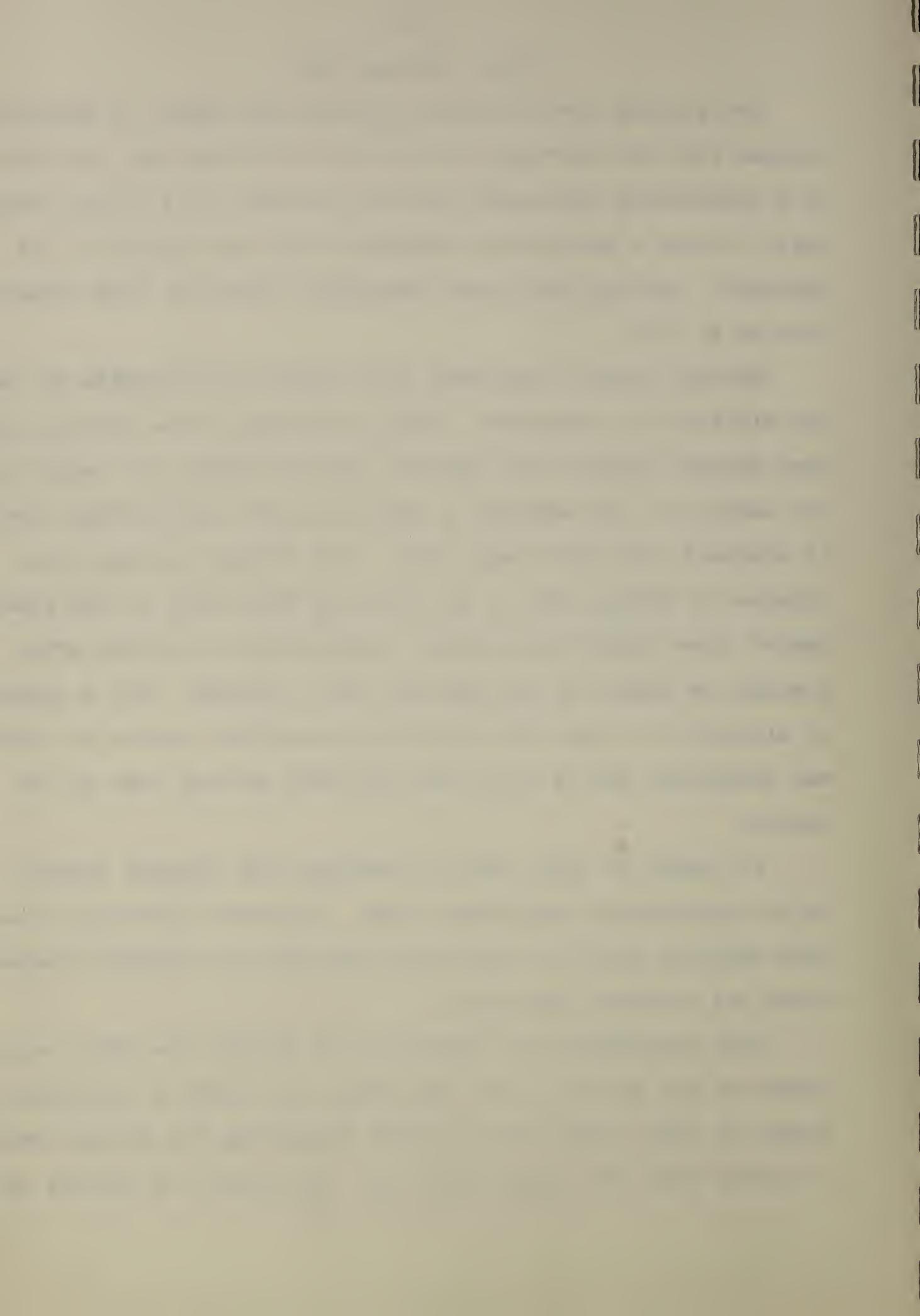
2.2.2 Setting Time

The setting time is defined here as the number of minutes elapsed from the starting of the mix to the time when the point of a penetrating instrument such as the point of a Gilmore needle fails to make a perceptible indentation on the surface of the specimen. Setting times were determined either at room temperature or at 37°C.

Setting times of mixtures that harden in 10 minutes or longer are difficult to determine. Often, the mass of the mixture almost hardens within a few minutes, but on placing the needle on the surface of the material a small but still perceptible circle is produced even after many hours. The initial setting times reported in Tables III, V, VI, VII, and VIII refer to the time period after which only a slight indentation is visible after placing the needle on the material for 5 seconds. For a number of mixtures the time after which no perceptible circle is visible was determined and is also shown as final setting time in the tables.

It should be noted that the setting time depends largely on the experimental conditions used. Therefore different values were obtained when the tests were conducted at different temperatures and relative humidities.

When information was desired as to whether the mixes would harden at all and if so, if they would set within a reasonable length of time, mixes were prepared containing the maximum amount of powder that the liquid would wet. The edge of a spatula was

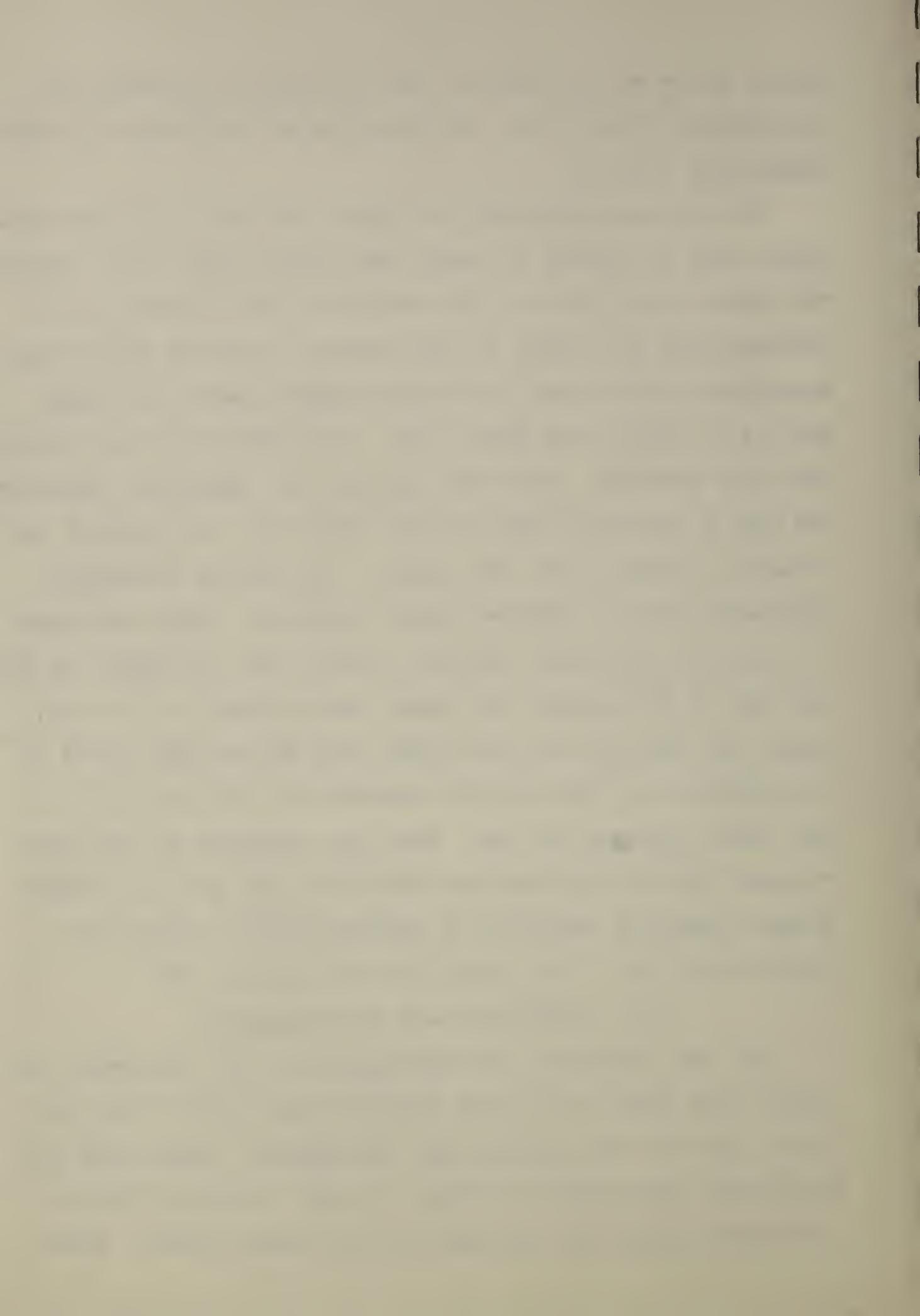


placed on the mix at various time intervals to determine the approximate setting time. Setting time was determined at room temperature ($27 \pm 2^\circ\text{C}$).

The setting times given in Tables III and V to X were determined using the amount of powder and liquid given in the tables. The powder-liquid ratios used were determined by previous experiments and give mixes of approximately standard consistency. Mixing was accomplished by placing weighed amounts of powder and 0.4 ml liquid on a glass slab. The powder was then divided into four portions. The first portion was completely incorporated with a stainless steel spatula before the next portion was brought in contact with the liquid. The mix was thoroughly spatulated until no unmixed powder remained. Since some mixes of standard consistency required a great deal of powder the mixing time to incorporate the powder varied from 2 to 4.5 min. Hence, the time at which the brass ring and mix was placed in an atmosphere of 100% relative humidity at 37°C was 3.5 ± 1.5 min. after starting the mix. With the exception of this modification the setting time was determined with a 1 lb standard Gilmore needle as described in American Dental Association Specification No. 9 for Dental Silicate Cements [2].

2.2.3 Solubility and Disintegration

For the solubility and disintegration test the powder and liquid were mixed in the same powder-liquid ratio by the procedure used for the setting time experiments. Since some experimental mixes adhere strongly to glass, pieces of Teflon were used between the specimens and the glass plates. After



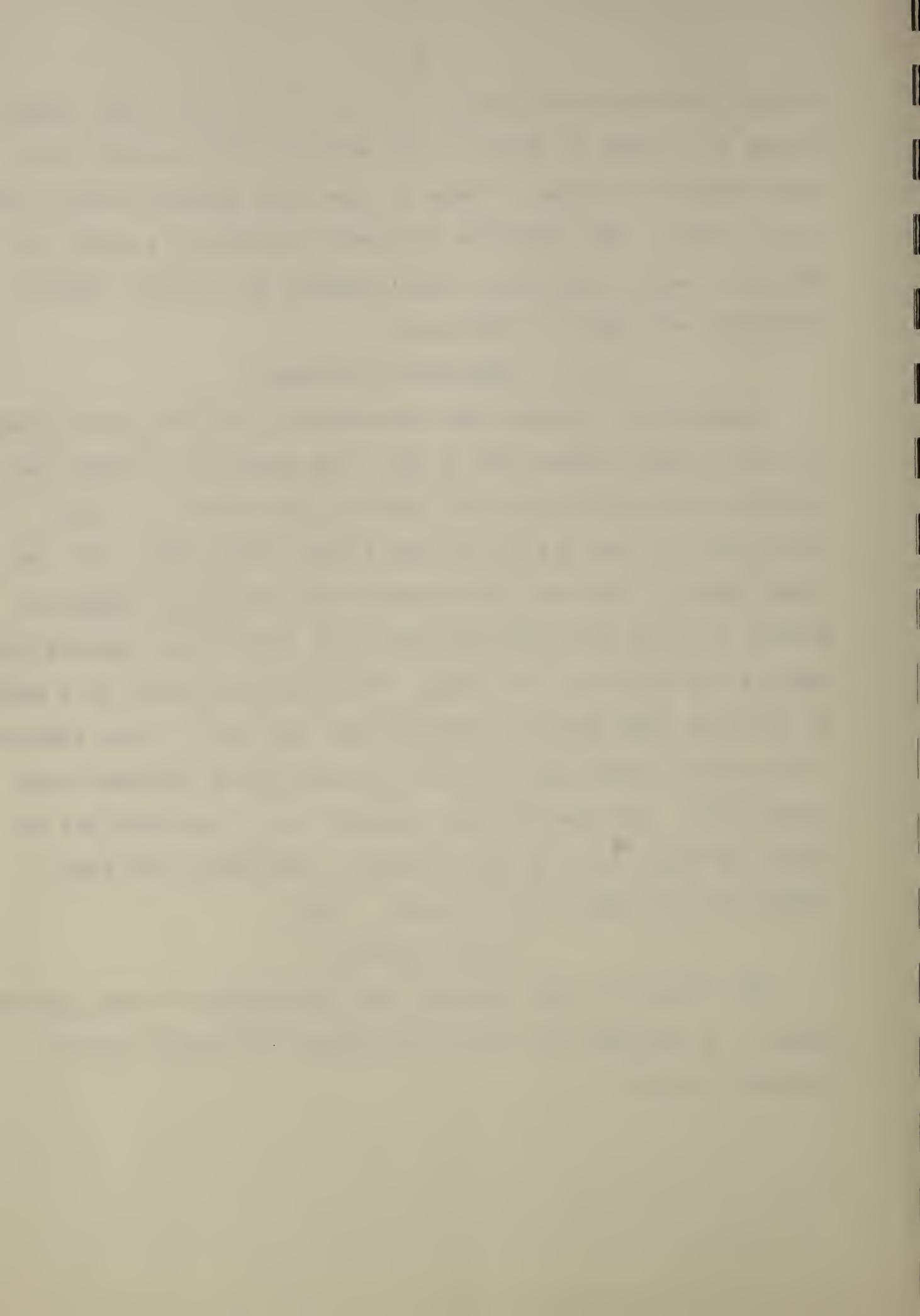
mixing the powder and liquid, 0.5 ml of the mixture was transferred to a piece of Teflon, 0.03 mm thick, and covered by a second piece of Teflon. These in turn were placed between two glass plates. The procedure followed thereafter is given in American Dental Association Specification No. 9 [2]. Determinations were made in duplicate.

2.2.4 Compressive Strength

Compressive strength was determined by the method outlined in A.D.A. Specification No. 9 [2]. The specimens, having the powder-liquid ratios given in Table V, were made 3 ± 2 min. after start of the mix by filling a hard rubber mold with the mixed cement. The ends of the mold were covered by pieces of Teflon, 0.03 mm thick and by flat glass plates held against the ends of the mold by a "C" clamp. The mold was placed in a bath at 37°C and 100% relative humidity for one hour. After removal of the glass plates and Teflon, the ends of the specimen were ground flat. The specimen was pressed out of the mold and immersed in water at 37°C for 23 hours. Specimens were then crushed at the rate of 370 lb/min. $\pm 10\%$.

2.2.5 Density

The density of the products was determined by using approximately 1 g specimen in a 50 ml pycnometer with water as displacement liquid.



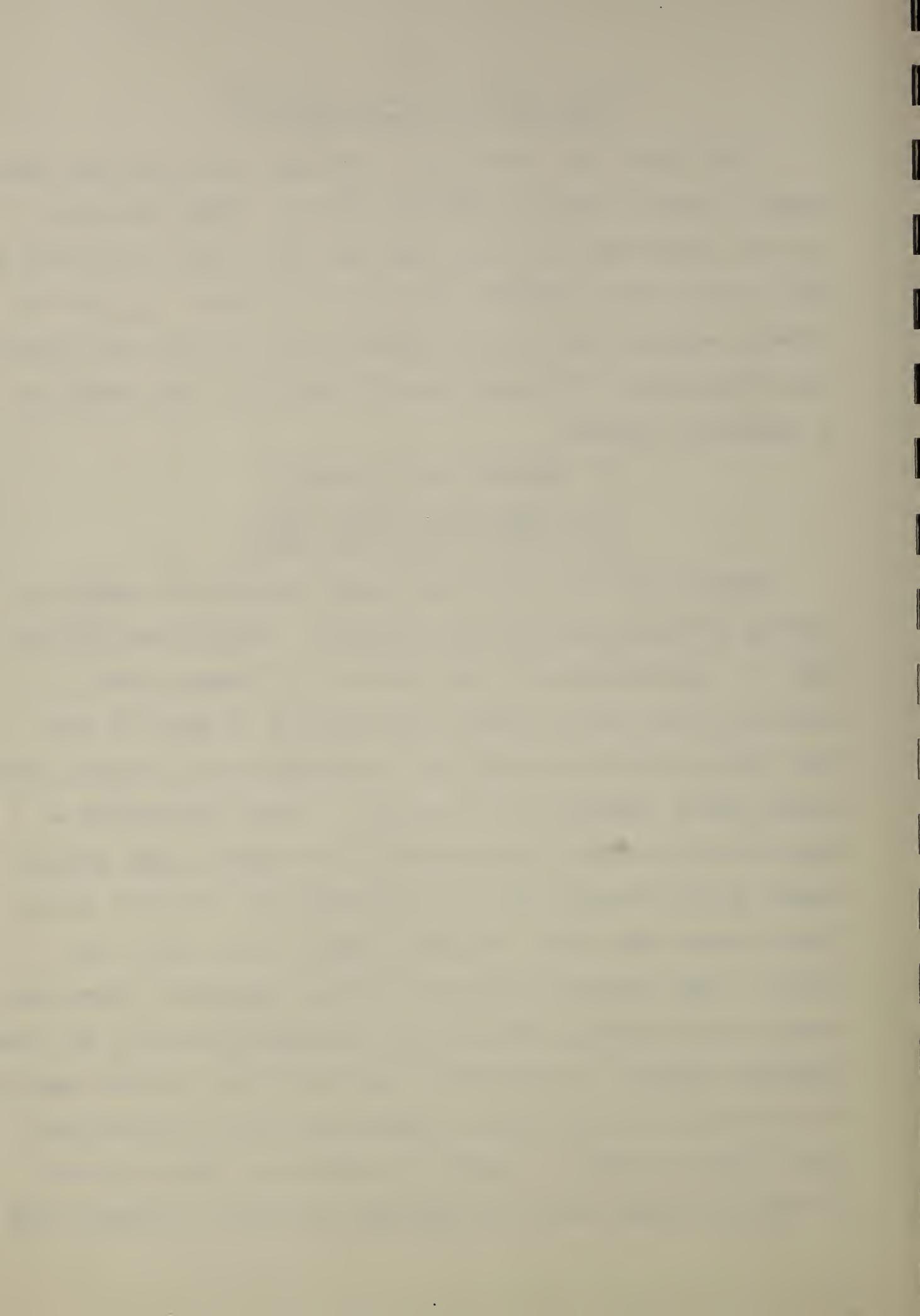
2.2.6 Effect of Zinc Oxide-EBA Products on Polymerization

A few tests were conducted to evaluate zinc oxide-EBA mixtures as cement liners for acrylic resins. Mixes containing various proportions of eugenol-EBA and zinc oxide were placed in split molds 6 mm in diameter and 12 mm in length. At time intervals ranging from 10 to 90 minutes after placing the cement, room temperature curing resin was put on top of the cement by a "paint-in" technic.

3. RESULTS AND DISCUSSION

3.1 Reaction of Zinc Oxide With Various Chelating Agents

Mixtures of zinc oxide and liquids that may be capable of forming chelated products were prepared. Results are given in Table I. o-Ethoxybenzoic acid reacts with reagent grade or Hyperfine zinc oxide to form a hard product in about 12 min. Zinc oxide-o-salicylaldehyde and -o-ethoxybenzoyl chloride mixtures harden fairly readily (1 to 2 hours). A small percentage of Hyperfine zinc oxide incorporated in the reagent grade greatly speeds up the setting time of o-ethoxybenzoyl chloride mixes. Similar mixes with other chelating agents do not show this effect. Some aliphatic chelating agents, especially those containing acidic groups (lactic acid, ethoxyacetic acid), and some compounds capable of enolization (acetylacetone) harden rapidly. The products are quite water soluble and usually disintegrate when placed in water. A number of compounds, such as esters of salicylic acid, ethyl acetoacetate, citraconic anhydride and



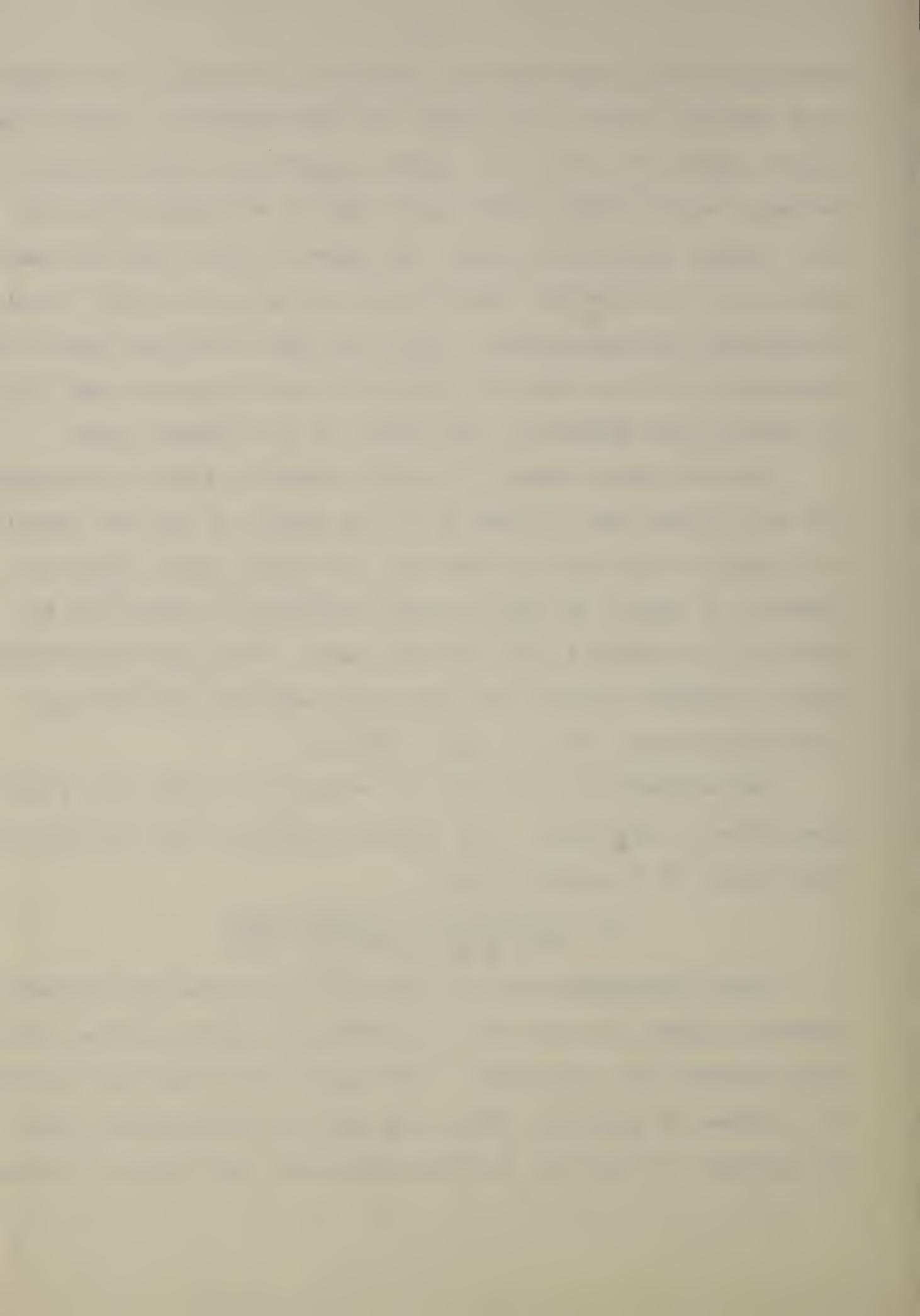
ethylenediamine, form coherent products of relatively low compressive strength after a few hours. At room temperature under atmospheric conditions, mixes of eugenol, isoeugenol, guaiacol and 2-methoxy-4-methylphenol harden more rapidly with Hyperfine than with reagent grade zinc oxide. It appears likely that the ammonia present in the Hyperfine material acts as an accelerator for mixes containing o-methoxyphenols. With the other chelating agents differences in setting time and properties of the product vary little on substituting Hyperfine zinc oxide for the reagent grade.

From the small number of liquid chelating agents investigated, few conclusions can be drawn as to the effect of various substituent groups on the setting reaction. An acidic group (COOH or phenolic or enolic OH under certain conditions) appears to be necessary to obtain a hard coherent mass. Thus, o-ethoxybenzoic acid or guaiacol harden with zinc oxide whereas veratrole (o-dimethoxybenzene) does not react readily.

The mechanism of the reaction between zinc oxide and ethylenediamine is not known. The product formed in this reaction is undoubtedly of a complex nature.

3.2 Reaction of Various Oxides with o-Ethoxybenzoic Acid

Since o-Ethoxybenzoic acid appeared to be the most effective chelating agent, a study of the reaction of various oxides with this compound was undertaken. The results are summarized in Table II. Oxides of group IIA (MgO, CaO, BaO) of the periodic table react rapidly to form hard brittle materials. The oxides of group IIB



(ZnO, CdO, HgO) form hard cohesive products as does lead oxide (litharge) in group IVB. The other oxides either do not react with o-ethoxybenzoic acid or form soft putty-like products.

Substituting magnesium oxide for zinc oxide in EBA mixes shortens the setting time and lowers compressive strength and increases considerably the solubility and disintegration (Table III). In air the product adheres strongly to glass.

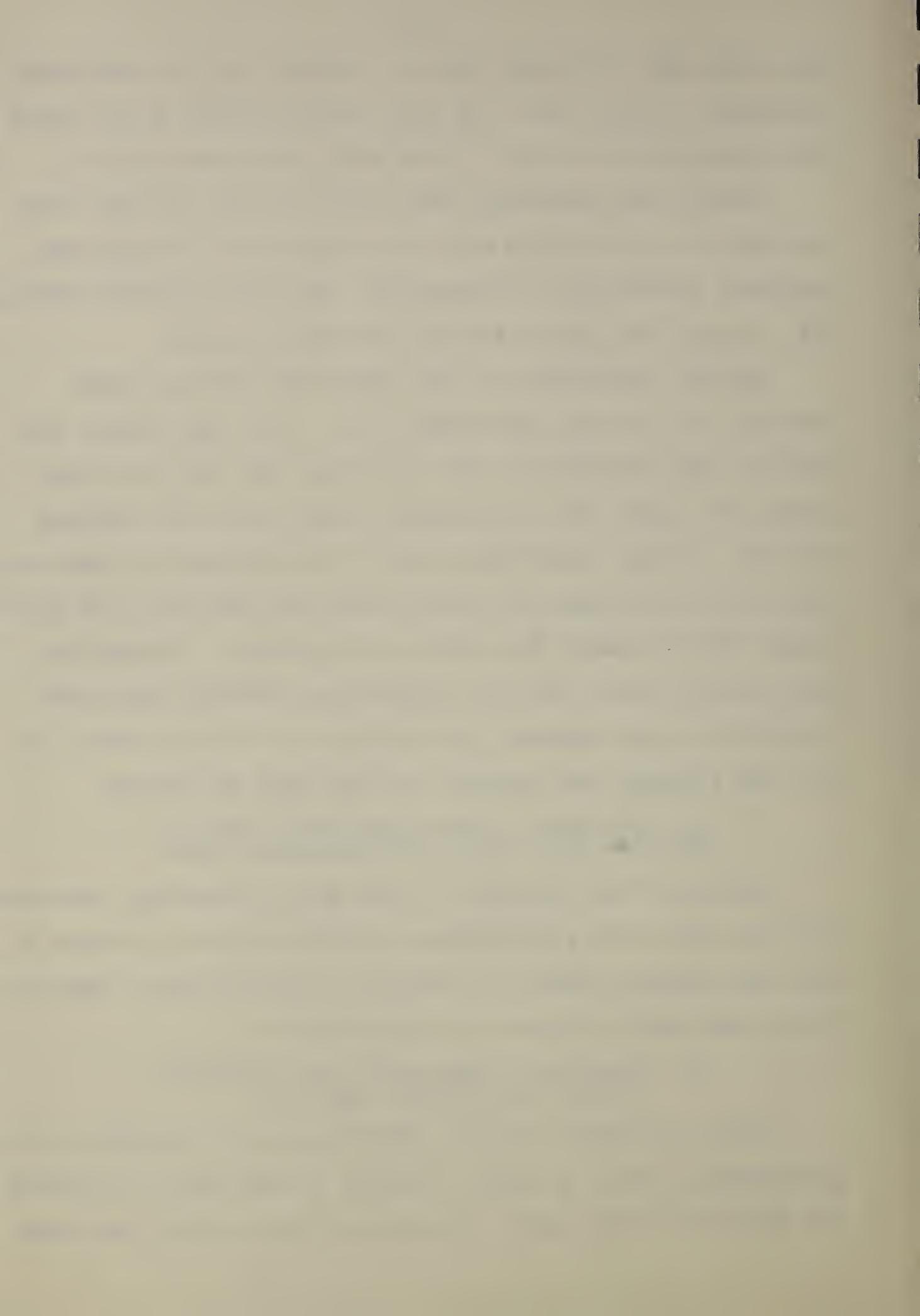
Partial replacement of zinc oxide with calcium oxide decreases the setting time (Table III). With some mixes, the setting time decreases to such an extent that not all of the powder and liquid can be thoroughly mixed before the mixture has set. Calcium oxide mixes result in an exothermic reaction. Where high percentages of calcium oxide are employed, the setting cement "boils" making the product very porous. Although no quantitative tests, with the exception of setting time, were conducted, it was apparent that addition of calcium oxide lowered the strength and resulted in high water solubility.

3.3 Reaction of Some Hydroxides, Halides and Zinc Salts with o-Ethoxybenzoic Acid.

Results of the reaction of some metal hydroxides, chlorides and zinc salts with o-ethoxybenzoic acid are given in Table IV. Only the products formed with mercuric chloride have a hard cohesive mass which, however, is quite brittle.

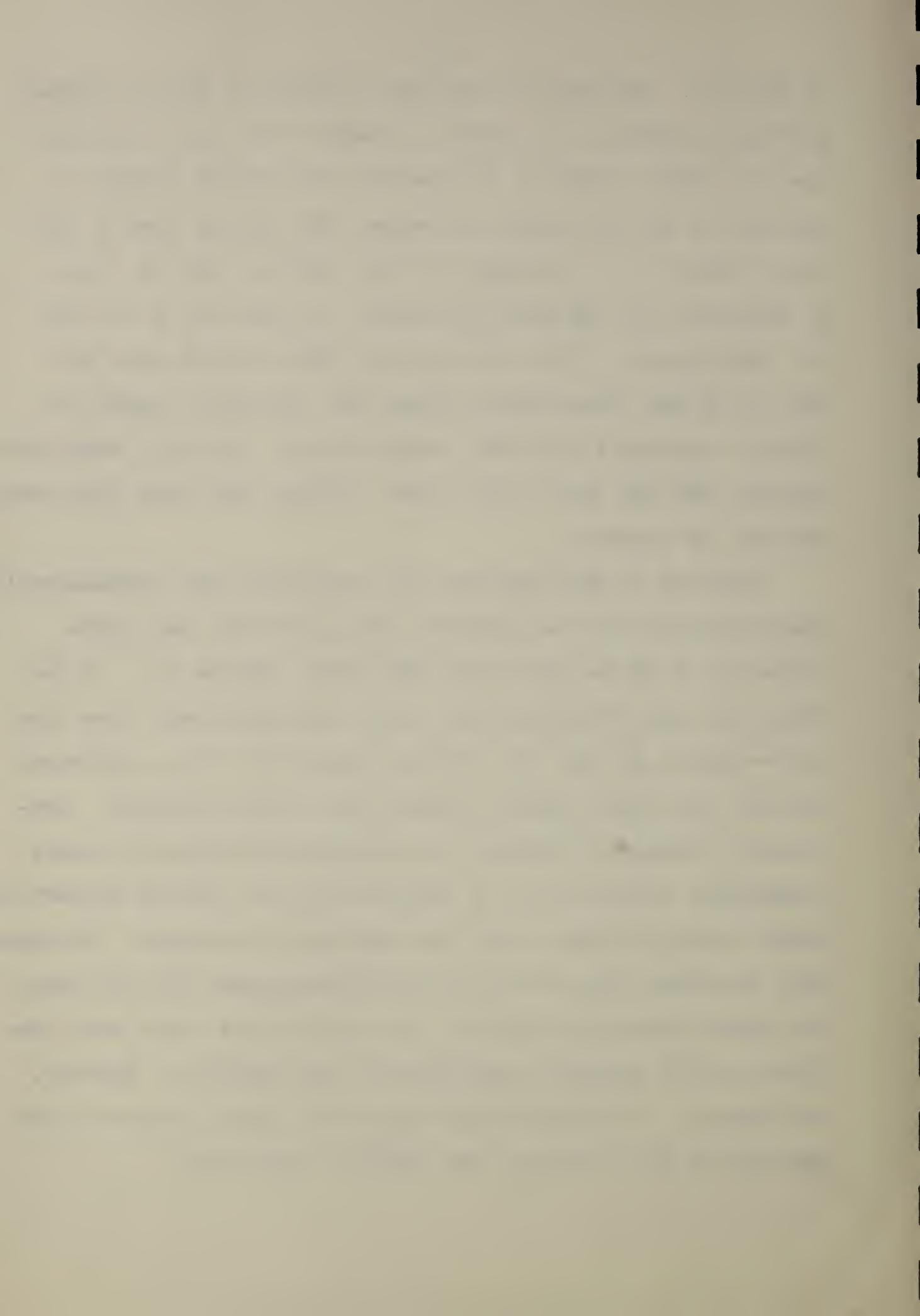
3.4 Reaction of Zinc Oxide with o-Ethoxybenzoic Acid-Eugenol Mixtures

Since preliminary studies showed that zinc oxide-EBA mixtures disintegrate slowly in water, a series of EBA-eugenol solutions was mixed with zinc oxide. Results of these studies are shown



in Table V. Addition of even small amounts of EBA to eugenol increases markedly the amount of powder that can be incorporated to obtain a mixture of standard consistency (Figure 1). Addition of EBA to eugenol decreases the setting time of the mixes (Figure 1). A minimum initial setting time of 3 min. is obtained with 25% EBA-75% eugenol as compared to 120 min. for 100% eugenol. The setting time remains short over the 20% to 70% EBA concentration range and increases rapidly on further increase in the EBA concentration. However, mixes containing 100% EBA show a much lower setting time than those containing 15% eugenol.

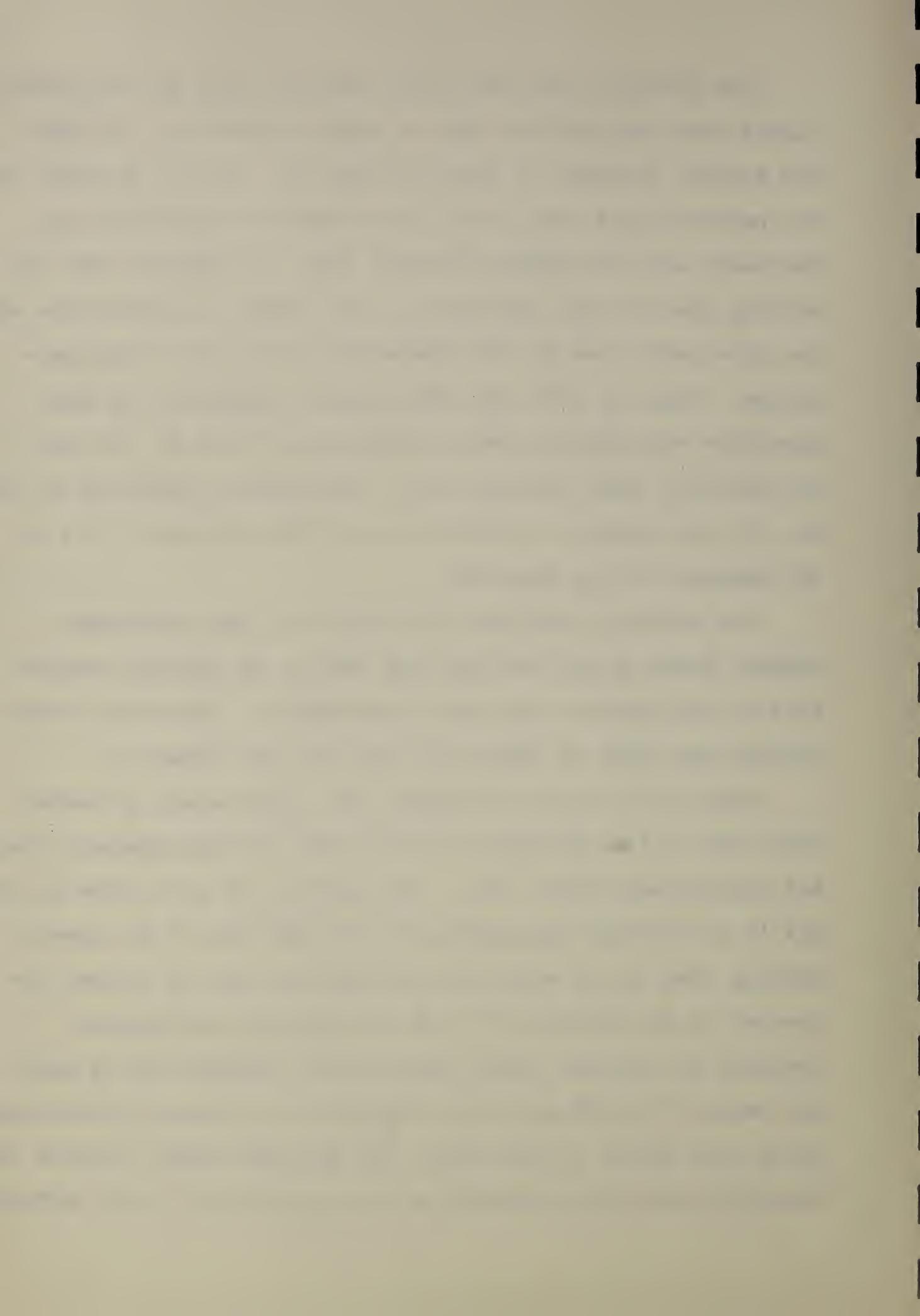
Addition of EBA increases the solubility and disintegration characteristics of the products from 0.10% for zinc oxide-eugenol to 7.9% for zinc oxide-EBA mixes (Figure 2). In the solubility and disintegration tests, specimens made from zinc oxide-eugenol and EBA give highly viscous tar-like substances whereas zinc oxide-eugenol cements give white residues. Compressive strength increases on incorporating EBA and reaches a maximum of 10,600 psi at a concentration of 75% EBA (Figure 2). Higher concentrations lower the compressive strength. The density increases from 2.68 for zinc oxide-eugenol to 3.31 g/ml for mixes containing 75% EBA. No quantitative tests were conducted on the adhesive properties of the products. However, the behavior of the materials during the tests indicates that addition of EBA increases the adhesive properties.



The effect of the zinc oxide particle size on the powder-liquid ratio and setting time of mixes containing a 75% EBA-25% eugenol solution is given in Table VI. It will be noted that the powder-liquid ratio used for a standard consistency mix decreases with decreasing particle size. It appears that the setting time is more dependent on the method of manufacture of the zinc oxide than on the dimensions of the zinc oxide particles. Thus, at 37°C and 100% relative humidity, the EBA-Hyperfine mix hardens slowly whereas zinc oxide No. 513 has the shortest final setting time. The greater reactivity of the No. 513 zinc oxide is probably due to the presence of 2.5 to 3% carbonate in the material.

The effect of addition of fillers to zinc oxide-EBA-eugenol mixes on the setting time and on the physical properties of the products was also investigated. Results of these studies are shown in Tables VII and VIII and Figure 3.

Addition of quartz increases the total amount of powder which can be incorporated to yield a mix of approximately standard consistency (Table VII). The quantity of zinc oxide in the mix is not altered appreciably by the addition of the quartz. Setting time of the mixes is shortened and can be further decreased by the addition of 0.6% zinc acetate accelerator. Products of slightly higher compressive strength with a maximum value of 11,600 psi were obtained for a mixture containing 69.2% zinc oxide, 30.8% quartz, 75% EBA-25% eugenol (Figure 3). Solubility and disintegration of the products is little affected



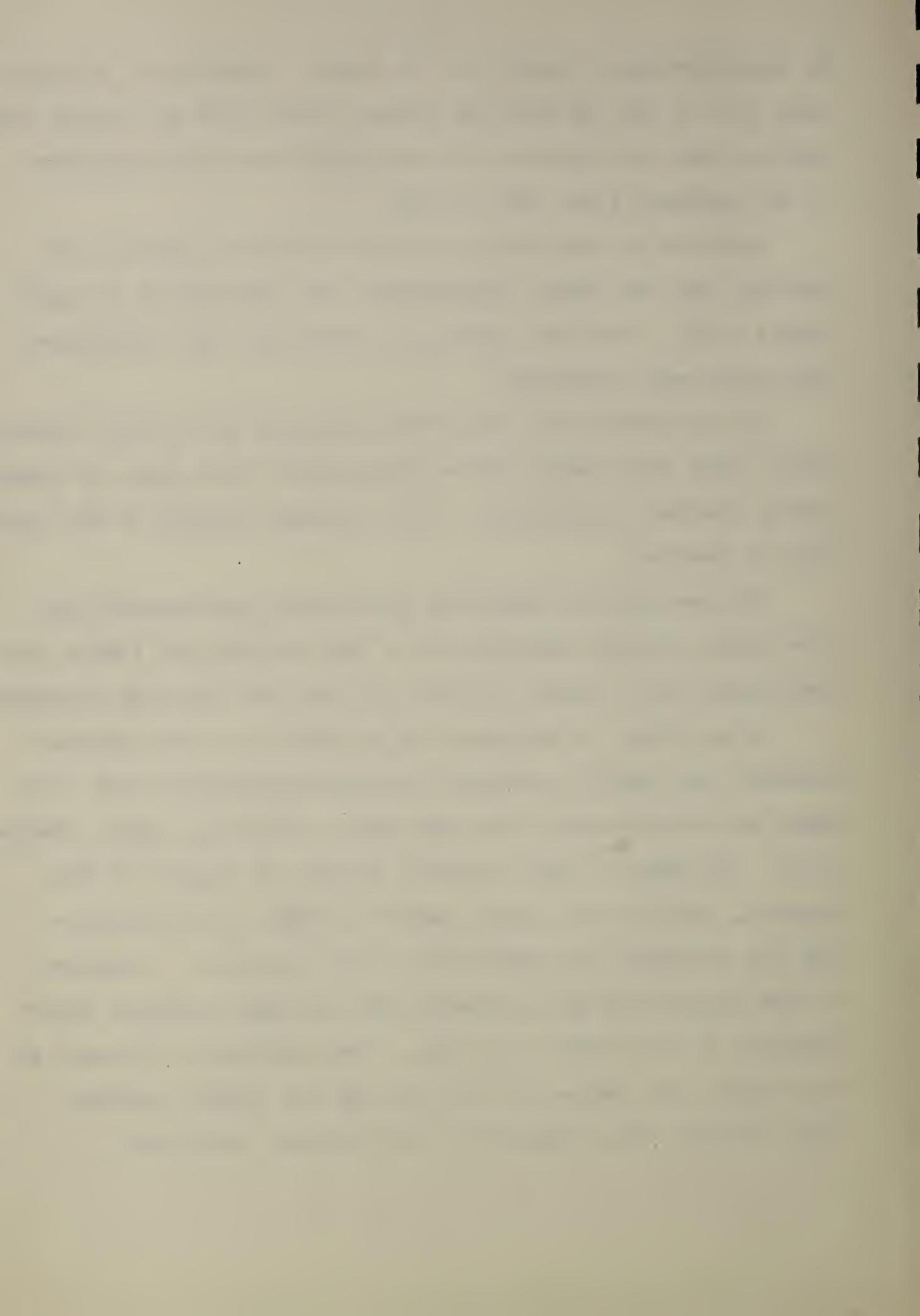
by incorporation of quartz in the mixes. Addition of 5% silicone R-23 to the 75% EBA-25% eugenol liquid does not change the setting time but decreases the solubility and disintegration of the products from 3.2% to 2.5%.

Addition of dark rosin as filler shortens slightly the setting time and lowers considerably the compressive strength (Table VIII). For this reason, no solubility and disintegration tests were conducted.

On the addition of tricalcium phosphate as a filler (Table VIII), much less powder can be incorporated into mixes of approximately standard consistency. The crushing strength of the product is lowered.

Calcium oxide or magnesium oxide when incorporated with zinc oxide, eugenol and EBA give a fast setting mix (Table VIII). The product has a smooth surface, but has low crushing strength.

In an effort to decrease the solubility of the hardened product, the readily available 2,4-dimethoxybenzoic acid (2,4-DMBA) was incorporated into some mixes containing quartz (Table VIII). 2,4-DMBA is only slightly soluble in eugenol or EBA. However, addition of a small amount of DMBA to 50% eugenol-50% EBA increased the solubility of the products. A mixture of 25% eugenol-75% EBA saturated with 2,4-DMBA hardened after addition of zinc oxide in 38 min. The compressive strength of the cement was lowered to 6500 psi and the cement appeared less adhesive when compared to the products containing



no 2,4-DMBA. Incorporation of small amounts of 2,4-DMBA did not lower the solubility.

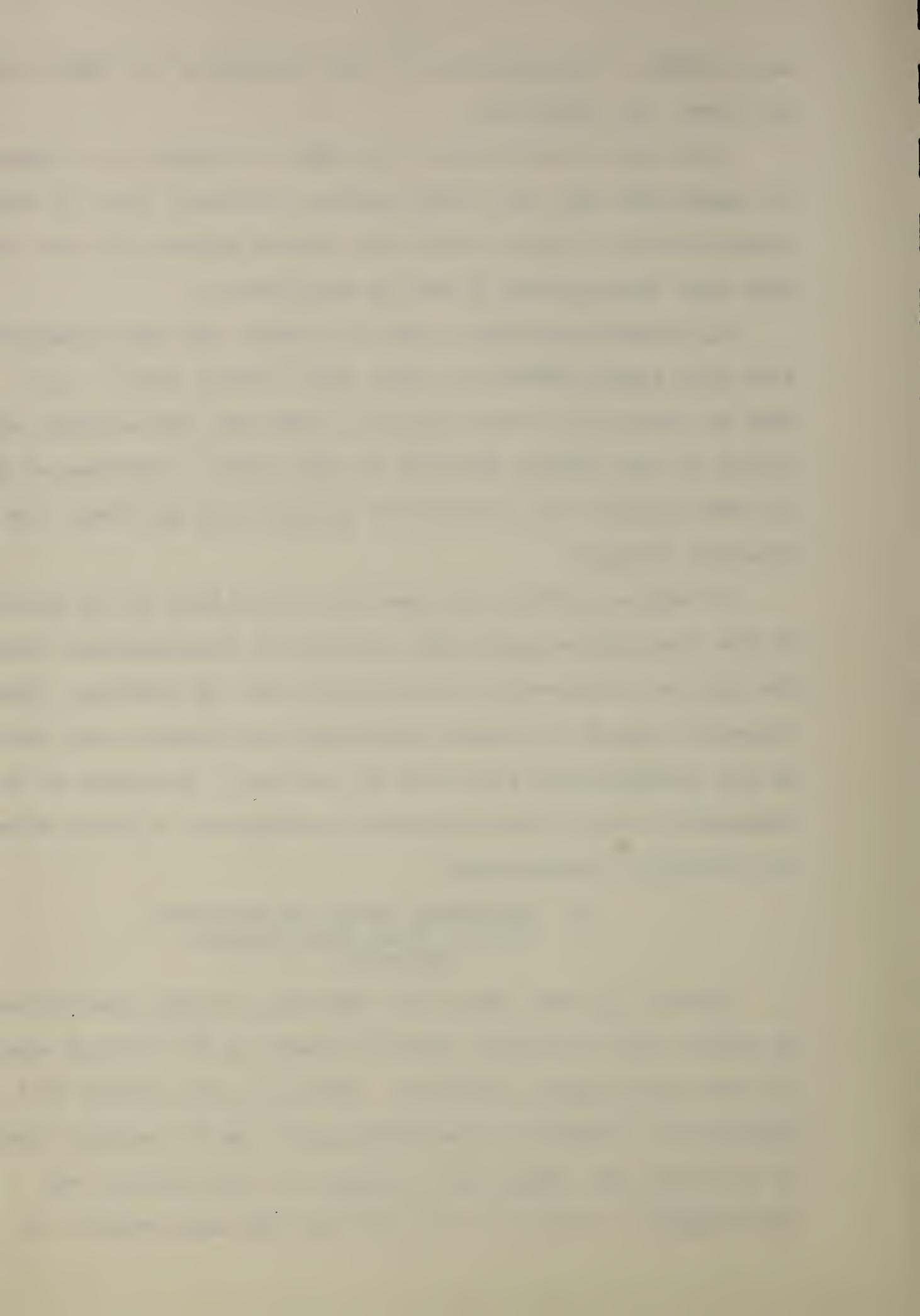
Addition of solutions of 2,4-DMBA in methanol or ethanol to eugenol-EBA and zinc oxide produced mixtures that did not harden within 18 hours, even when liberal amounts of zinc acetate were incorporated to act as accelerator.

2,3-Dimethoxycinnamic acid (2,3-DMCA) was also incorporated into eugenol-EBA-zinc oxide mixes (Table VIII). 2,3-DMCA is soluble in either eugenol or EBA and can be mixed with either or both before addition of zinc oxide. Addition of 1% 2,3-DMCA appears to increase the setting time and lower the crushing strength.

It may be possible to lower the solubility of the products of the zinc oxide-eugenol-EBA reaction by incorporation into the mixture tailor-made ethoxybenzoic acid derivatives. Such compounds should be liquids containing hydrophobic side chains at the unsubstituted positions of the ring. Synthesis of such compounds in this laboratory and investigation of their effect on setting is contemplated.

3.5 Chelating Agents as Accelerators of Zinc Oxide-Eugenol Mixtures

Crowell [3] has shown that addition of small quantities of acetic acid to eugenol greatly speeds up the setting reaction of zinc oxide-eugenol mixtures. Therefore, the effect of a 5% addition of a number of chelating agents on the setting times of the mixes and compressive strength of the products was investigated. Results of the setting time measurements at



37°C and 100% relative humidity are given in Table IX. Addition of acetic acid or a chelating agent increases the amount of powder that can be incorporated in the mix. All compounds, with the exception of ethylenediamine, accelerate the reaction. Compounds containing carboxylic acid groups give the shortest setting times. The compressive strength of the products is low.

The effect of addition of acetic acid or chelating agents to EBA is less pronounced (Table X). Addition of these compounds lowers the powder-liquid ratio as well as the setting time.

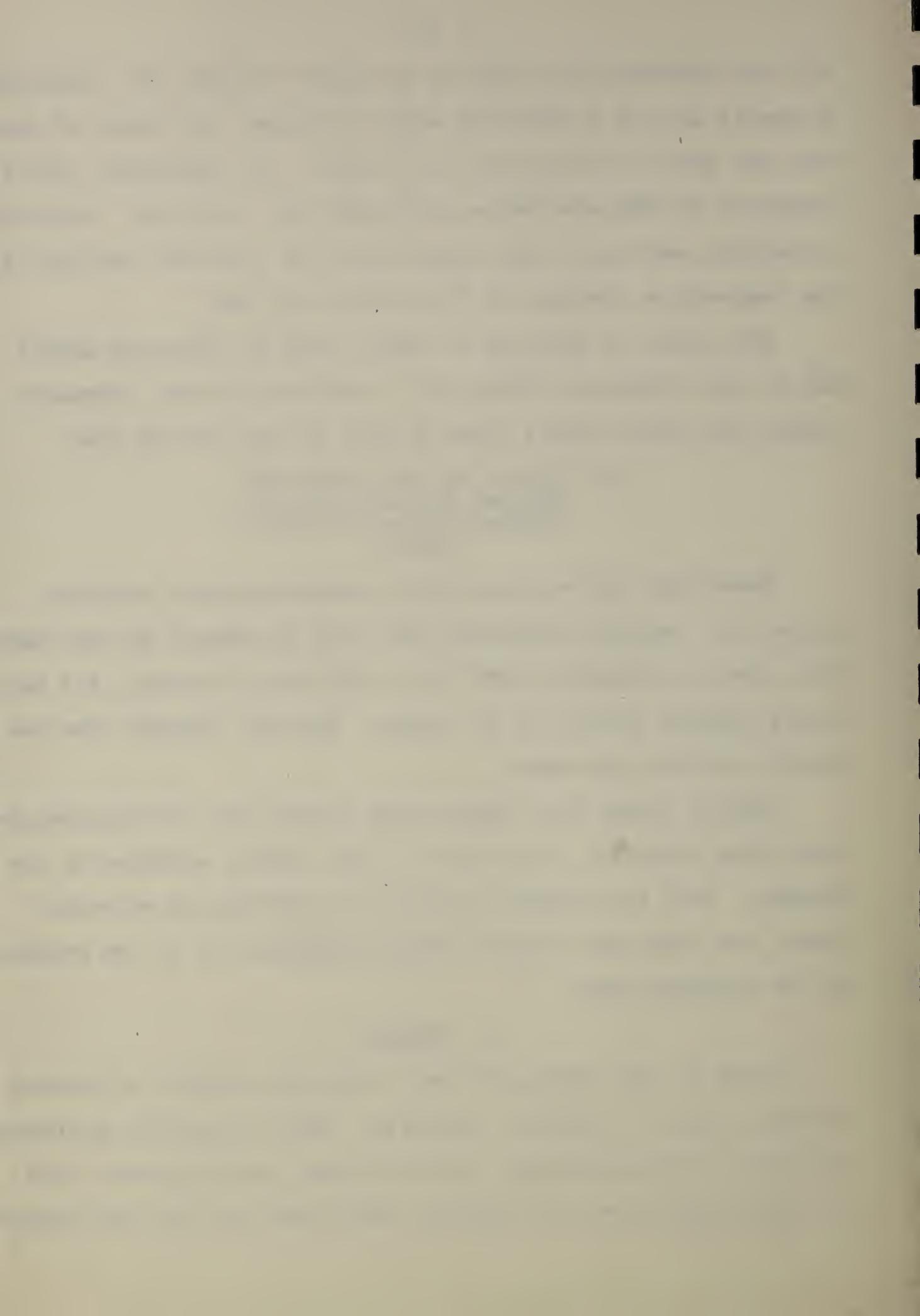
3.6 Effect of Zinc Oxide-EBA-Eugenol Mixtures on the Polymerization of Acrylic Resins

Commercial self-curing acrylic monomer-polymer slurries placed over cements containing more than 5% eugenol do not harden. With cements containing 100% EBA or 95% EBA-5% eugenol, the acrylic slurry hardens rapidly in all cases. However, monomer from the acrylic softens the cement.

Acrylic resins also harden when placed over salicylaldehyde-zinc oxide mixtures. The cement is not readily attacked by the monomer. When this cement is placed in cavities of extracted teeth, the teeth are stained yellow, probably due to the presence of the aldehyde group.

4. SUMMARY

Mixes of zinc oxide with many compounds capable of forming chelates result in coherent products. Mixes containing o-ethoxybenzoic acid, salicylaldehyde, acetylacetone, o-ethoxyacetic acid or lactic acid form hard products within one hour at room tempera-



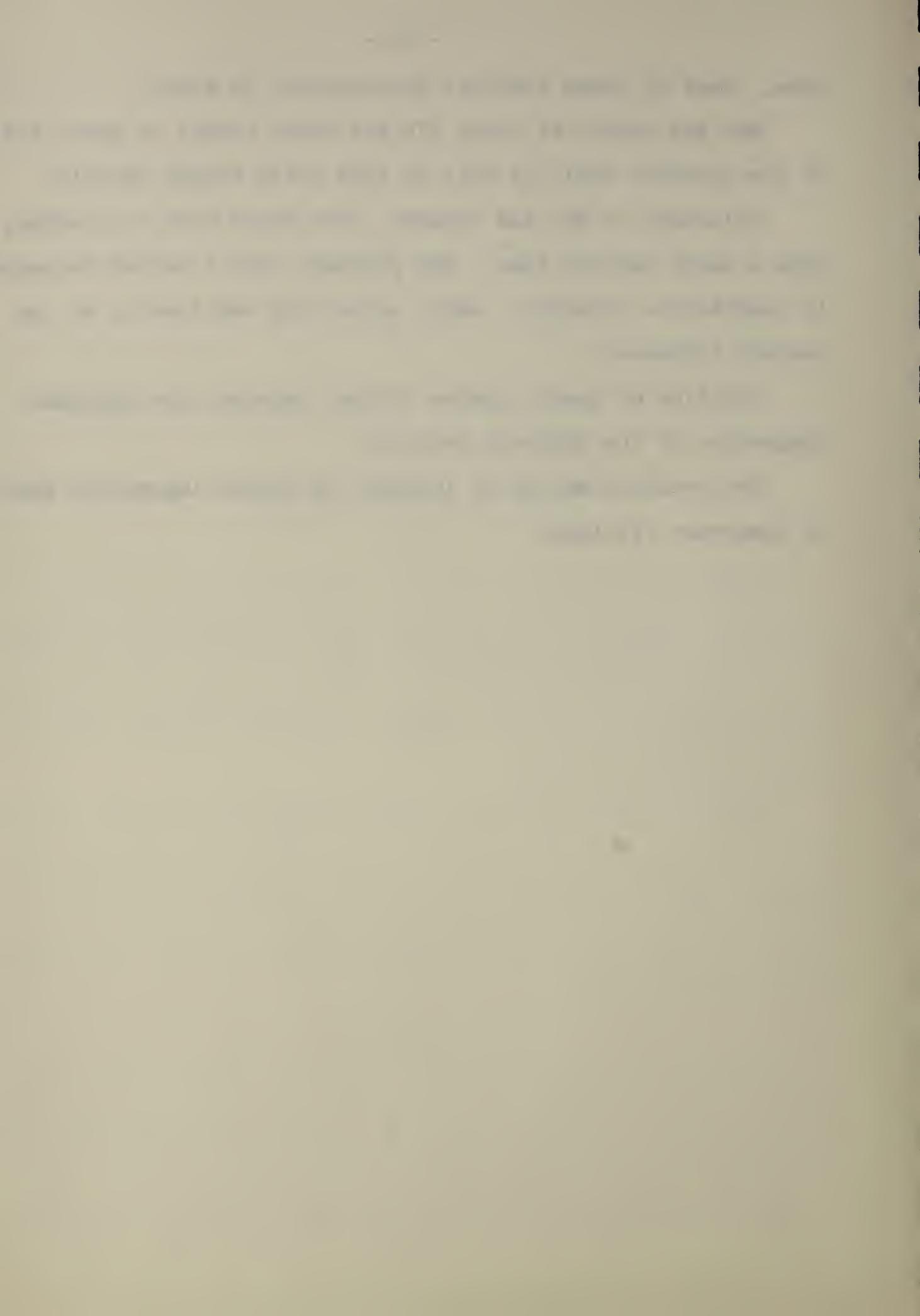
ture. Some of these products disintegrate in water.

EBA and oxides of group IIB and those tested in group IIA of the periodic table as well as lead oxide harden rapidly.

Solutions of EBA and eugenol, when mixed with zinc oxide, have a short setting time. The products show a marked increase in compressive strength. Water solubility and density of the product increases.

Addition of quartz powder further improves the physical properties of the hardened material.

The products may be of interest as dental impression pastes or temporary fillings.



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Table I

Reaction of Zinc Oxide with Chelating Agents
at Room Temperature

Chelating Agent	Grade of Zinc Oxide	Approximate Setting Time	Properties of Product
eugenol	RG (a)	3 hrs	
isoeugenol	HF (b)	1.5	
<u>isoeugenol</u>	RG	(c)	
<u>isoeugenol</u>	HF	3	reddish, hard
guaiacol	RG	(c)	
guaiacol	HF	1	reddish, hard
2-methoxy-4-methylphenol	RG	16	hardens, slightly putty-like
2-methoxy-4-methylphenol	HF	2	fairly hard
<u>o</u> -ethoxybenzoic acid	RG	0.2	colorless, hard
<u>o</u> -ethoxybenzoic acid	HF	0.2	reddish, hard
<u>o</u> -ethoxybenzoyl chloride	RG	<1	yellow, fairly hard adhesive
<u>o</u> -ethoxybenzoyl chloride	HF	<1	reddish, sticky
<u>o</u> -ethoxybenzoyl chloride	95% RG 5% HF	0.03	yellow, hard, brittle
methyl salicylate	RG	<20	colorless, cake, crumbly
methyl salicylate	HF	<20	reddish, soft
ethyl salicylate	RG	<18	colorless, coherent crumbles
ethyl salicylate	HF	(c)	

Table I (Continued)

Chelating Agent	Grade of Zinc Oxide	Approximate Setting Time	Properties of Product
		hrs	
<u>isoamyl</u> salicylate	RG	(c)	
<u>isoamyl</u> salicylate	HF	(c)	
<u>o</u> -salicylaldehyde	RG	1	yellowish-green, hard
<u>o</u> -salicylaldehyde	HF	2	brown, hard
<u>o</u> -methoxybenzaldehyde	RG	>70	greyish, putty-like
<u>o</u> -methoxybenzaldehyde	HF	(c)	
<u>o</u> -methoxyphenyl acetate	RG	(c)	
<u>o</u> -methoxyphenyl acetate	HF	(c)	red cake
<u>o</u> -nitroanisole	RG	(c)	
<u>o</u> -nitroanisole	HF	(c)	
veratrole	RG	>70	colorless, soft, coherent
veratrole	HF	(c)	
<u>o</u> -hydroxyacetophenone	RG	(c)	
<u>o</u> -hydroxyacetophenone	HF	<24	reddish, soft coherent cake
ethyl acetoacetate	RG	4	colorless, soft coherent cake
ethyl acetoacetate	HF	(c)	
ethyl benzoylacetate	RG	(c)	
ethyl benzoylacetate	HF	(c)	
acetylacetone	RG	0.02	colorless, hard

Table I (Continued)

Chelating Agent	Grade of Zinc Oxide	Approximate Setting Time hrs	Properties of Product
acetylacetone	HF	0.02	reddish, hard
citraconic anhydride	RG	1	chalky, coherent
citraconic anhydride	HF	(c)	soft coherent cake
lactic acid	RG	0.5	colorless, hard, disintegrates in water
lactic acid	HF	0.75	reddish, hard
pyruvic acid	RG	0.01	yellow, very brittle
pyruvic acid	HF	0.01	not cohesive, white fumes are given off during the reaction
ethoxyacetic acid	RG	<1	hard, brittle, adhesive
ethoxyacetic acid	HF	<1	reddish, hard, adhesive, disinte- grates in water
ethylenediamine	RG	2	colorless, fairly hard, brittle
ethylenediamine	HF	4	reddish, fairly hard, brittle
tetrahydroxyethyl- ethylenediamine	RG	(c)	
tetrahydroxyethyl- ethylenediamine	HF	(c)	

(a) Reagent grade.

(b) Hyperfine.

(c) Does not harden appreciably in 24 hours.

Table II

Reaction of Various Oxides with o-Ethoxybenzoic Acid
at Room Temperature

Material	Approximate Setting Time min	Properties of Product
Copper oxide	(b)	soft, putty-like
Silver oxide	(b)	no apparent reaction
Magnesium oxide	3	white, hard, brittle
Calcium oxide	<1/2 ^a	grey, very brittle
Barium monoxide	<1/2 ^a	pink-grey, hard, brittle
Zinc oxide (reagent)	11	hard, adhesive
Cadmium oxide	2-6	dark brown, hard
Mercuric oxide (yellow)	2-15	orange, hard, brittle
Mercuric oxide (red)	4	red, hard
Aluminum oxide	(b)	soft, putty-like
Titanium oxide	(b)	soft, putty-like
Stannic oxide	(b)	grey-white, cohesive, putty-like
Lead monoxide (litharge)	1/2	hard, yellow
Lead dioxide	(b)	black, soft, putty-like
Arsenic trioxide	(b)	soft, sticky, putty-like
Bismuth trioxide	(b)	greenish yellow, soft, putty-like
Molybdenum trioxide	(b)	soft, putty-like
Manganese dioxide	(b)	sticky, putty-like

Table II (Continued)

Material	Approximate Setting Time	Properties of Product
		min
Ferric oxide	(b)	soft, putty-like
Cobaltic oxide	(b)	black, putty-like
Nickelous oxide	(b)	green, cohesive, putty-like
Nickel dioxide	(b)	black, cohesive, putty-like

a Highly exothermic reaction.

b Does not harden appreciably within 24 hours.

Table III

Reaction of Various Oxides with o-Ethoxybenzoic Acid

Temperature: 37°C

Relative Humidity: 100%

Oxide	Standard Consistency	Initial Setting Time	Solubility and Disintegration	Compressive Strength
	g/0.4 ml	min	%	psi
ZnO	2.30	13-24	7.97	7200
MgO	0.65	3.5	48.5	low
75% MgO - 25% ZnO		3.5		low (brittle)
50% MgO - 50% ZnO	0.97	4.0	30.9	450
25% MgO - 75% ZnO		5.5		
CaO		0.5		
75% CaO - 25% ZnO		1.0		
50% CaO - 50% ZnO		1.0		
15% CaO - 85% ZnO		9.0		
10% CaO - 90% ZnO		40.0		
10% CaO - 50% MgO 40% ZnO		3.0		

Table IV

Reactions of Various Compounds with *o*-Ethoxybenzoic Acid
at Room Temperature

Material	Approximate Setting Time hrs	Properties of Products
<u>Hydroxides</u>		
Lithium hydroxide	-	not very cohesive, fairly hard
Calcium hydroxide	(b)	not coherent ^a
Strontium hydroxide	(b)	soft, putty-like
<u>Halides</u>		
Sodium chloride	(b)	no apparent reaction
Magnesium chloride	(b)	no apparent reaction
Calcium chloride	75	mixture crumbles
Mercuric chloride	<24	hard, brittle
Lead chloride	(b)	yellow, putty-like
<u>Zinc salts</u>		
Zinc acetate	(b)	grey-white, cohesive, putty-like
Zinc oxalate	(b)	soft, cohesive, putty-like
Zinc sulfate	(b)	no apparent reaction

a Exothermic reaction.

b Does not harden appreciably within 24 hours.

Table V

Physical Properties of α -Ethoxybenzoic Acid-Eugenol-Zinc Oxide Mixtures

Temperature: 37°C Relative Humidity: 100%

Composition (a)		Powder used for 0.4 ml of liquid	Setting Time	Solubility and disin- tegration	Compressive Density Strength
Solid	Liquid	g	min	%	psi g/ml
ZnO	100% EBA	2.30 (b)	13-24	88	7.97 7,200
ZnO	95% EBA 5% Eugenol	2.35 (b)	13	182	
ZnO	90% EBA 10% Eugenol	1.90 (b)	60	1040	
ZnO	85% EBA 15% Eugenol	1.95 (b)	95	860	
ZnO	80% EBA 20% Eugenol	2.20 (b)	30	95	
ZnO	75% EBA 25% Eugenol	2.25 (b)	18	35	3.21 10,600
ZnO	70% EBA 30% Eugenol	2.20 (b)		7.0	21
ZnO	62.5% EBA 37.5% Eugenol	2.20 (b)		6.5	13

Table V (Continued)

Composition (a)		Powder used for 0.4 ml of liquid	Setting Time min	Solubility and disin- tegration %	Compressive Strength psi	Density g/ml
Solid	Liquid	g	min	%	%	
ZnO	50% EBA	2.20 (b)	4.0	5.5	2.31	4,400
	50% Eugenol					
ZnO	25% EBA	1.70	3.0	3		
	75% Eugenol					
ZnO	17.5% EBA	1.75	3.5	8		
	82.5% Eugenol					
ZnO	10% EBA	2.10 (b)	16	33		
	90% Eugenol					
ZnO	100% Eugenol	1.30 (b)	120	540		
	100% Eugenol (Commercial product)	1.40 (b)	-	8	0.1	3,000
ZnO	99.5% ZnO 0.5% Zn(Ac) ₂	EBA 2.30	10	43	-	-
	Guaiacol	1.6	60	-	0.076	-

a Percentage by weight for solids and by volume for liquids.

b Powder-liquid ratio that yields mix of standard consistency.

Table VI

Setting Times of EBA-Eugenol Solutions with Zinc Oxides of Varying Particle Size

Temperature : 37°C
Relative Humidity: 100%
Liquid : 75% EBA
 25% Eugenol

Grade of Zinc Oxide	Average Diameter of Particle (a)	Surface Area (a)	Standard Consis- tency	Setting Time	Remarks	
	microns	m ² /g	g/0.4ml	Initial min	Final min	
Reagent	-	-	2.30	24	88	--
XX-78	.3	4	2.15	26	72	--
Kadox-72	.2	6.5	2.05	34	77	--
Kadox-15	.1	10	1.80	36	81	--
USP	--	--	1.60	34	70	--
Micronized USP	--	--	2.70	25	81	--
No. 513	0.04	31	0.25	26	54	very brittle
Hyperfine	.02	--	0.50	55	113	--

(a) Values given by the manufacturer.

Table VII

Physical Properties of o-Ethoxybenzoic Acid-Eugenol-Zinc Oxide-Quartz Mixes

Composition (a)						Temperature : 37°C Relative Humidity : 100%	Compressive Strength	Density
Solid			Liquid	Powder used for 0.4 ml liquid	Setting Time	Solubility and disintegration		
ZnO	Quartz	EBA	Eugenol	g	min	%	g/ml	
69.2	30.8	100	---	3.20	10.0	19	9,200	
69.2	30.8	80.0	20.0	3.00	6-11	51	10,700	
69.2	30.8	75.0	25.0	3.25	8.0	32	11,600	
69.2	30.8	70.0	30.0	3.00	5-10	21	10,200	
69.2	30.8	62.5	37.5	3.00	4.5-7	7	9,200	
68.8	30.6	75.0	25.0	2.60	4.0		10,300	
+0.6%Zn(Ac) ₂								
67.2	29.8	75.0	25.0	2.70	3.0		8,000	
+3%Zn(Ac) ₂								
69.2	30.8	75.0	25.0	3.25				
+5.0% Silicone R-23								
100	---	72.5	22.5				6,900	
+5% Silicone R-23								

(a) Percentage by weight for solids and by volume for liquids.

Table VIII

Physical Properties of o-Ethoxybenzoic Acid-Eugenol-Zinc Oxide Mixes Containing Various Additives

Composition (a)		Powder used for 0.4 ml of liquid	Initial Setting Time	Solubility and disin- tegration	Compressive Strength
Solid	Liquid	g	min	%	psi
69.2% ZnO 30.8% $\text{Ca}_3(\text{PO}_4)_2$	75.0% EBA 25.0% Eugenol	1.08			6,000
81.8% ZnO 19.2% Rosin	75.0% EBA 25.0% Eugenol	2.75			4,400
50.0% ZnO 50.0% MgO	50.0% EBA 50.0% Eugenol		6.5		
50.0% ZnO 50.0% MgO	50.0% EBA 50.0% Eugenol		3		low
75.0% ZnO 25.0% MgO	25.0% EBA 75.0% Eugenol			28	
40.0% ZnO 50.0% MgO 10.0% CaO	50.0% EBA 50.0% Eugenol		5.5		
40.0% ZnO 50.0% MgO 10.0% CaO	50.0% EBA 50.0% Eugenol		4		
66.0% ZnO 33.0% Quartz 1.0% -DMCA	72.7% EBA 27.3% Eugenol		2.20	12.5	7,800
68.8% ZnO 30.6% Quartz 0.6% $\text{Zn}(\text{Ac})_2$	50.0% EBA 50.0% Eugenol + 2,4-DMBA			3.7	
69.2% ZnO 30.8% Quartz	75.0% EBA 25.0% Eugenol sat. with 2,4-DMBA		2.25	38	6,500

(a) Percentage by weight for solids and by volume for liquids.

Table IX

Properties of Zinc Oxide-Eugenol Mixtures Containing
Acetic Acid or Chelating Agents

Temperature : 37°C
Relative Humidity: 100%

Eugenol	Composition of Liquid	Powder used per 0.4 ml liquid	Final Setting Time	Compressive Strength
%	%	g	min	psi
100	,	1.30	540	3000
99.5	0.5, acetic acid	2.25	12	1800
95	5 acetic acid	2.25	6	3500
95	5 ethoxyacetic acid	2.35	12	2400
95	5 lactic acid	2.25	24	----
95	5 acetylacetone	2.35	73	----
95	5 ethyl acetoacetate	2.25	90	----
95	5 ethylenediamine	2.25	>200	----

Table X

Setting Times of Zinc Oxide-EBA Mixtures
Containing Acetic Acid or a Chelating Agent

Temperature : 37°C
Relative Humidity: 100%

Composition of liquid: 95% EBA
5% Additive

Additive	Powder used per 0.4 ml liquid	Final Setting Time
	g	min
EBA	2.30	88
Acetic Acid	1.20	35
Ethoxyacetic Acid	1.90	55
Acetylacetone	2.00	57
Ethylenediamine	2.10	>60

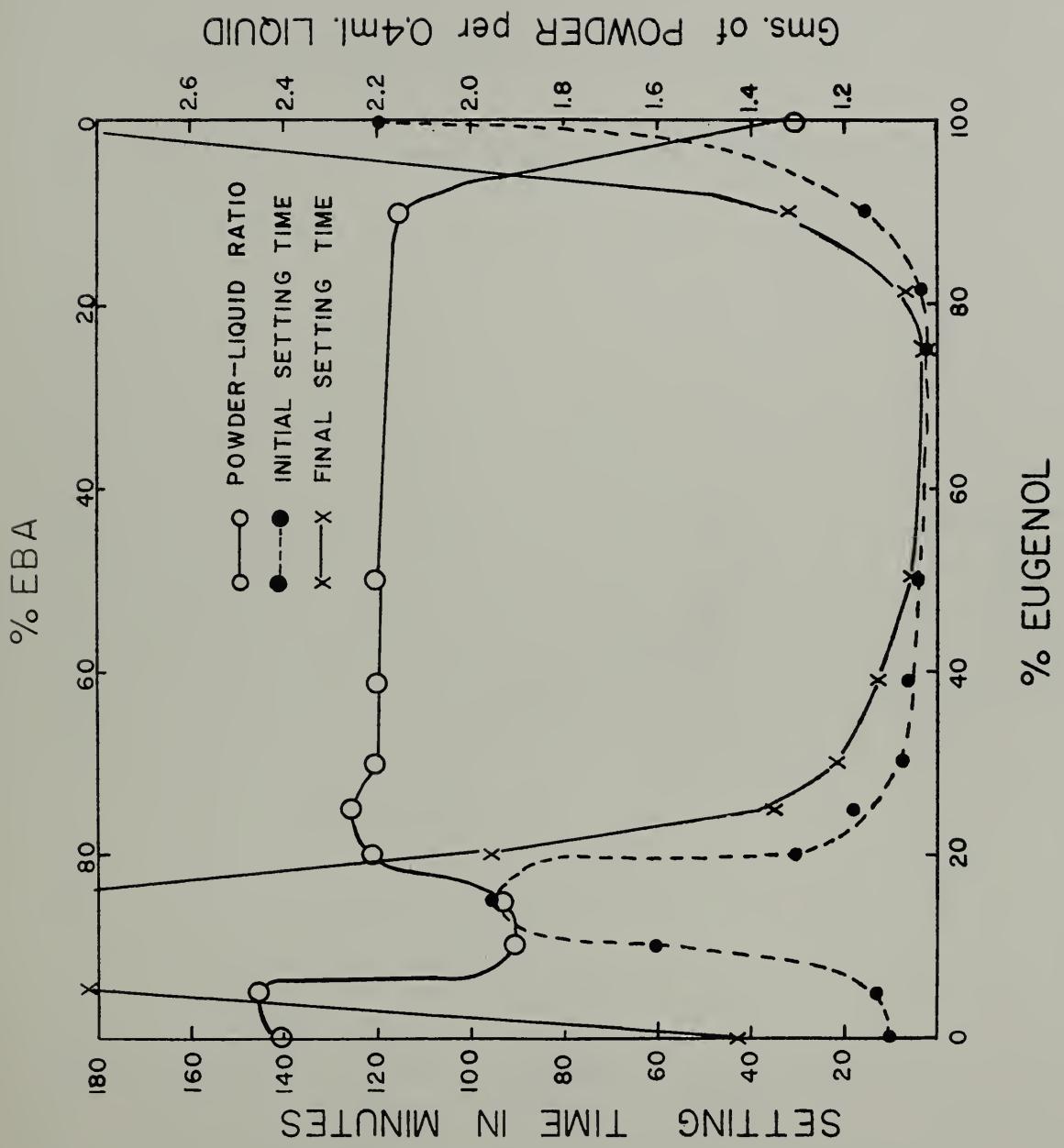


Figure 1. Setting time and powder-liquid ratio of zinc oxide-EBA mixes.

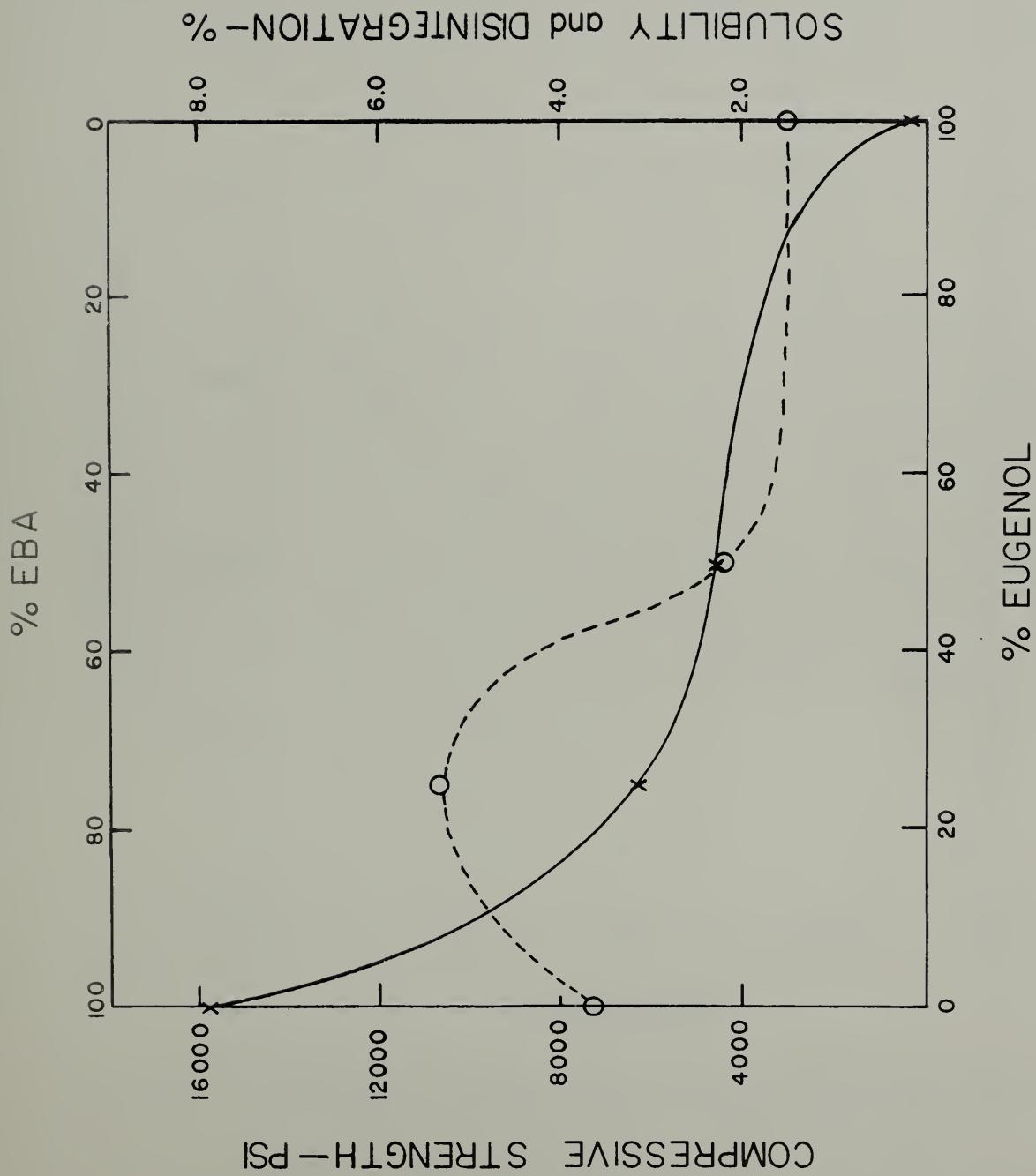


Figure 2. Compressive strength and solubility and disintegration of zinc oxide -EBA mixtures.

—x— Compressive strength.
 —o— Solubility and disintegration.

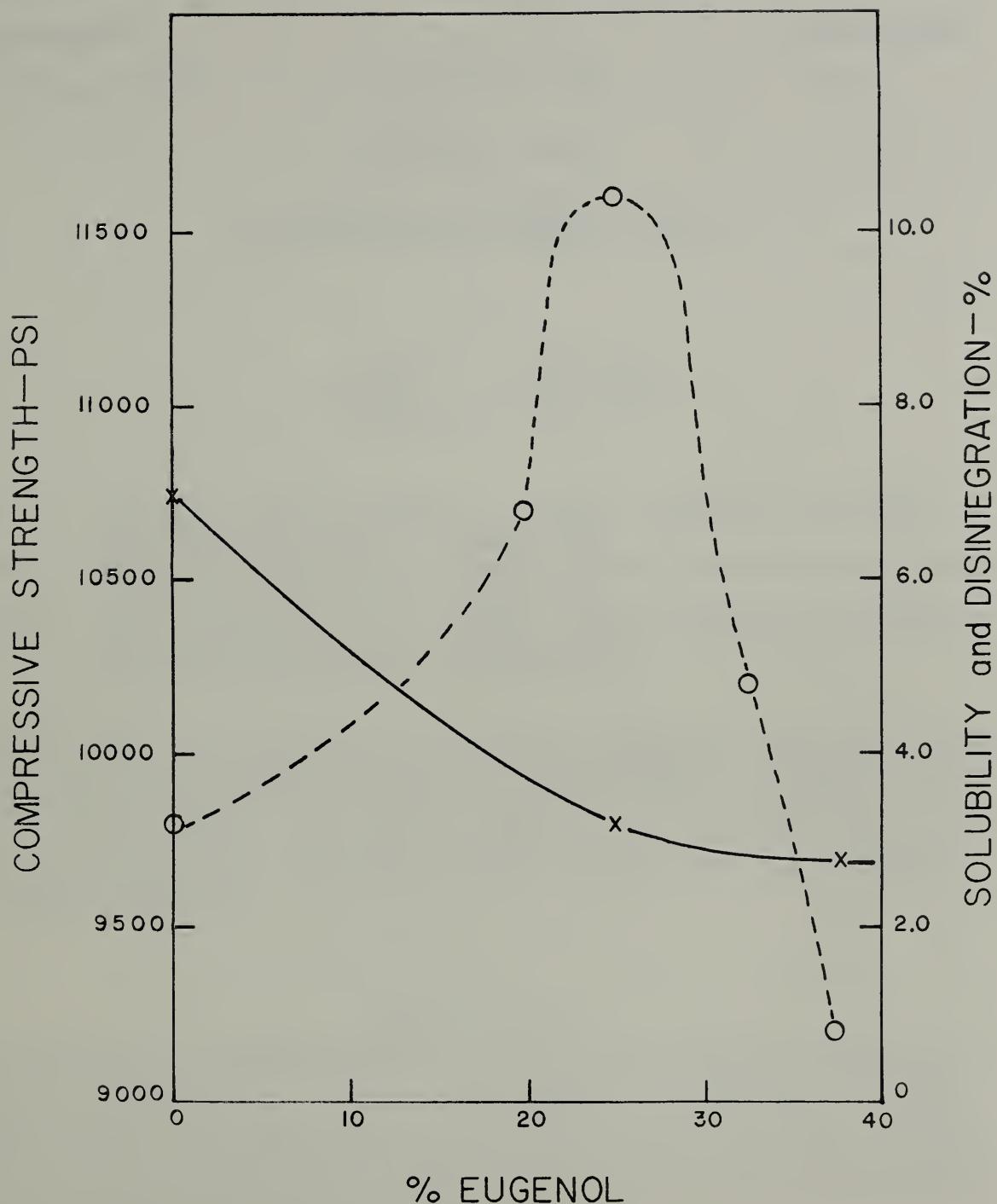


Figure 3. Compressive strength and solubility and disintegration of zinc oxide - quartz - EBA - eugenol mixtures.

Powder: 69.2% ZnO - 30.8% quartz.
 Liquid: EBA - eugenol.

○ - - - ○ compressive strength.
 X — X solubility and disintegration.

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Progress Report

PHYSICAL PROPERTIES OF CHROMIUM-COBALT DENTAL ALLOYS

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U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

PHYSICAL PROPERTIES OF CHROMIUM-COBALT DENTAL ALLOYS

Abstract

The chemical composition and some physical properties of a group of commercial chromium-cobalt dental alloys have been investigated. Spectrographic and wet chemical analyses were made and liquidus temperature, hardness and various tensile properties were determined.

As others have reported, it was found to be desirable to use threaded enlarged-end specimens rather than straight rods for tensile tests. In addition to the expected variation in properties between alloys, considerable difference was found between lots of a single alloy cast by various laboratories. Use of a controlled atmosphere furnace was required for liquidus temperature determinations because the alloys react readily with oxygen. A vacuum furnace, suitable for use with very small samples, was developed and employed for this purpose.

1. INTRODUCTION

The first patent on the chromium-cobalt alloys was obtained by Elwood Haynes in 1907 [1]. However, it was not until 1937 that R. W. Erdle and C. H. Prange of the Austenal Laboratories perfected the materials and techniques for the

use of these alloys in dental applications [2]. Since their introduction into dentistry, the chromium-cobalt alloys have made steady gains in popularity until, at present, the great majority of all partial dentures are made of material of this type. This increased use can be attributed to their low density, low material cost, and high modulus of elasticity in comparison to gold alloys.

This paper gives the results of tests of the physical properties of six commercial alloys, obtained by use of specimens comparable in size to dental appliances. The properties determined were: tensile strength, modulus of elasticity, yield strength, percent elongation, superficial hardness, and liquidus temperature.

Several studies of these alloys have been made in relation to their dental application. In addition to the work of Erdle and Prange; Paffenbarger, Caul, and Dickson at the National Bureau of Standards[3] and Bush, Ingersoll, and Peyton at the University of Michigan [4] have made special contributions to the field. The manufacturers of commercial dental alloys have compiled significant data on their own products. It was felt, however, that additional information was required to define the properties to be expected of currently available products and to serve as the basis for a proposed specification for these materials. It was also desired to investigate the reported superiority of the threaded

enlarged-end specimen to the straight rod specimen for tensile tests of these materials and to compare the properties of specimens of these materials as cast by various laboratories under what they ostensibly believe to be the best conditions.

The six alloys tested include five American products and one popular European alloy. The American materials were selected to give a representative sample of the products on the market at the present time. The group included new products as well as established products which had been tested previously. The European alloy selected has been used with some success by the armed forces in Europe and is believed to be typical of the better products available there.

These products can be divided into two classes on the basis of their composition. The first, containing approximately 60% cobalt and the second, less than 45% cobalt. Table 1 shows the composition of the alloys tested. Of the two alloys with less than 45% cobalt, the one with the high iron content, (Alloy C), has been withdrawn from the market since the start of this project.

2. EXPERIMENTAL PROCEDURE

In the course of this study, two types of specimens were employed. In the preliminary investigation, cast rods 0.09 inch in diameter and five to six inches in length were used; however, with this specimen design it was difficult to produce complete castings without interior porosity. Bush, Ingersoll,

and Peyton developed a threaded enlarged-end specimen design resembling the A.S.T.M. standard specimen but of a size corresponding more closely to dental applications. This specimen, as adapted for this study, consisted of a 0.09 ± 0.01 inch diameter rod, filleted to 12-24 threads at each end (Figure 1). Wax patterns were made at the National Bureau of Standards and distributed to the various laboratories which prepared specimens for use in the investigation. The specimens were cast according to the method normally employed in each laboratory. The resulting castings were then submitted to the National Bureau of Standards where all testing was done. Except for Alloy F (the European product), castings were made by the manufacturers of each alloy, the Central Dental Laboratory of Walter Reed Army Medical Center, Fifth Army Central Dental Laboratory at Saint Louis, Dental Division of the 7100th USAF Hospital, and the Dental Research Section of the National Bureau of Standards.

The tensile properties were determined on a 2000-pound capacity pendulum-type testing machine. The head speed employed was 0.02 inch per minute on the driven head, equivalent to a loading rate of 12,500 psi/min. in the elastic range. The strain was read from two Tuckerman optical strain gages by means of an autocollimator. Figure 2 shows the tensile specimen in the testing machine grips with the Tuckerman gages mounted opposite each other.

A load, approximately equivalent to a stress of 10,000 psi, was applied to the specimen and the strain read. The load was then increased to that equivalent to 50,000 psi and the strain again recorded. Thereafter the load was applied continuously and the strain was recorded at 25 pound load increments (approximately 4,000 psi) up to 500 pounds. The gages were then removed and loading was resumed at the same rate until the specimen failed.

The modulus of elasticity was calculated on the basis of the total strain between the stresses of 10,000 and 50,000 psi.

The yield strength, for purposes of this study, was defined as the higher stress of the first stress increment (approximately 4,000 psi) that produced a strain equal to or greater than 1.25 times that produced by an equal increment below 50,000 psi.

A one-inch gage length was used for the determination of the percent elongation. The length between the gage marks was measured to the nearest 0.002 inch both before testing and after reassembly following fracture.

The Rockwell 30N hardness was determined on specimens of the type used for the tensile test. Parallel flats were wet ground on opposite sides of the specimen. The use of a coolant during the grinding operation is essential in order to avoid changes in the hardness that otherwise would result

from the heat produced by the grinding. The brale indenter and 30 kg load employed in the Rockwell 30N test produce small enough indentations to allow a series of indentations along the longitudinal axis of the ground specimen in both the threaded and the rod portions. A study was made of the relative hardness so determined on specimens as cast and on the fragments of the specimens broken in the tensile test.

These materials, like most alloys, exhibit a melting range rather than a definite melting point. Because these alloys are to be cast, the liquidus temperature, the lowest temperature at which they are completely liquid, is of practical importance. Liquidus temperatures were determined using samples of approximately 35 grams of the alloy. These materials react very rapidly with oxygen at high temperatures and it is necessary to protect them during the prolonged heating required for accurate determinations. Commercial practice employs protective slags and short melting cycles, neither of which could be employed in this case. Since contamination can also occur from the refractories, they must be selected with care. Graphite, for example, must be excluded from the system to prevent the absorption of carbon by reaction with carbide-forming components. Vacuum melting was found to be superior to controlled atmospheres of nitrogen or argon in supplying the melt with the surface protection that slags provide in commercial melting practice.

The melting was done in a high frequency induction furnace which permitted rapid heating and produced a stirring action

which assisted in maintaining the homogeneity of the molten metal. The chrome-cobalt alloy in small ingots was held in a 19 mm o.d. x 90 mm alundum thimble. This was enclosed in a 35 mm i.d. Pyrex envelope and the intervening space was filled with 90 mesh alundum powder (Figure 3). The upper portion of the tube held a platinum-platinum rhodium thermocouple coiled and weighted in such a manner as to allow the protection tube containing the hot junction to move downward as the metal melted. An alundum plug covered the top of the thimble and acted as a guide through which the protection tube passed. The thermocouple passed through a seal in the upper portion of the glass to an ice-bath cold junction, and the resulting potential was measured on a potentiometer readable to 0.001 millivolt (Figure 4). The liquidus temperature was obtained from several cooling curves on each of two or more specimens of each alloy. The thermocouple was calibrated at the freezing points of copper and of Mond nickel.

3. DISCUSSION OF RESULTS

The physical properties of cast tensile specimens are dependent upon many factors and show considerable variation among the alloys tested. The resultant stress-strain curve, however, is typical of most non-ferrous materials. Figure 5, taken from a representative test of a clinically acceptable alloy, shows the generally favorable properties attained with these alloys. The modulus of elasticity was about 28,500,000 psi, which is

approximately twice that of gold alloys. The yield strength was about 70,000 psi and, since no constant stress yielding was observed, some arbitrarily selected method must be chosen for its calculation. The method employed (see above) was one that has been used for cast gold alloys (5). The tensile strength was approximately 105,000 psi.

In addition to the variation in properties that occurs between different alloys, considerable variation can occur in the measured properties for a single alloy when cast under different conditions. Table 2 shows the range of values obtained on alloy A for rod specimens cast by the manufacturer, and for threaded specimens cast by three separate laboratories each using their own techniques and procedures. The observed variation probably results from such factors as burn-out procedure, sprue size and arrangement, and melting and casting technique. Similar variation in the properties of alloy B are shown in Table 3. In this case, the difference in modulus of elasticity for individual specimens is particularly noteworthy. This property normally is not affected much by variations in processing but, in these two lots of castings, the individual modulus values ranged from 23.1×10^6 to 33.1×10^6 psi. This has been attributed to a tendency for this alloy to form grains approximating the diameter of the specimen used in this study. The wide range in the results can then be explained on the basis of anisotropy of the individual grains and their orientation relative to the specimen axis.

Table 4 gives the data for six alloys tested. All values were determined as described above except those for alloy F which were determined in accordance with the proposed specification (6) for these products. This specification employs a combined test for yield strength and modulus of elasticity similar to that in the Federal and American Dental Association specifications for casting golds (7, 8). As a result, the reported value of 60,000 psi yield strength is a minimum value only and the 29.0×10^6 psi modulus is a minimum value which is exact only if none of the specimens tested had proportional limits below 60,000 psi.

The composition of alloys E and F as given in Table 1 are those reported by the manufacturers. Chemical composition for alloys A - D was determined by analyses made on the specimens employed in the tensile tests, and represent the composition of the metal actually cast rather than that of the alloy as received from the manufacturer. Considering the melting practices employed, however, the differences are expected to be small. The analytical methods employed are described in references 9, 10 and 11. No attempt was made to make any correlation of the observed properties with composition. The number of compositions tested was small in relation to the number of elements present, so such a correlation would be of little value. In addition, there is good evidence in the results that other factors are of equal or greater importance. Examination of Table 1 shows that alloys D and E are of very similar composition, while Table 4 shows extreme variation in their properties, tensile strength and percent elongation in particular.

Rockwell Superficial Hardness (30N) was determined for each alloy along the entire length, both rod and threaded portions, of specimens used in the tensile test. This aided in the comparison of various sprung arrangements in regard to their ability to prevent formation of shrinkage porosity. As can be noted from Table 4, the results indicated a consistently higher hardness for the rod portion than for the threaded ends. This may be attributed to two possible causes, work hardening of the rod portion during the tensile test, or to structural differences in the two areas resulting from differences in their cooling rates. In order to determine which of these was the proper explanation, a series of hardness tests was performed on specimens which had not been tested in tension. The results are compared with those for previously pulled specimens in Table 5. It can be seen that there is no significant difference between the two groups.

In all probability, the small amount of elongation obtained in these alloys is insufficient to produce work hardening except in the immediate area of fracture. The observed difference in hardness between the rod and threaded portions of the specimens, therefore, is attributed to differences in grain size and distribution of micro-constituents. On the basis of these observations, it is concluded that hardnesses can be determined on the specimens after they have been tensile tested without introducing additional error.

A certain number of specimens were examined metallographically but, aside from the typical dendritic nature of the microstructures, no features were produced with sufficient regularity to permit correlation of structure with observed properties. This lack of correlation is a logical result of the wide range of casting procedures employed by the participating laboratories.

The liquidus temperature of the alloys tested fall into two groups apparently correlated with their cobalt content (Table 6). Alloys B, D, E and F, all containing approximately 60% cobalt, have liquidus temperatures between 2560° and 2650°F; while Alloy A, containing 43.5% cobalt, has a liquidus temperature of 2355°F. Alloy C had been withdrawn from the market, and no sample was available at the time the liquidus temperature determinations were made. The accuracy of the determined values for the liquidus temperature is believed to be within $\pm 10^{\circ}\text{F}$, and to be somewhat better in most cases. In cases where the desirability of greater accuracy would justify the use of larger specimens and greater expenditure of effort the methods reported by Roeser and Wensel (12) are recommended.

4. SUMMARY

The tensile strength, modulus of elasticity, yield strength, percent elongation, superficial hardness, and liquidus temperature were determined for a series of six commercial chromium-cobalt base dental casting alloys. The average tensile properties for these alloys fell within the following ranges: tensile strength 84,500 - 108,500 psi, modulus of elasticity 26.0 -

29.5×10^6 psi, yield strength 49,500 - 64,500 psi, and percent elongation 1.9 - 6.0%. The average Rockwell 30N hardness of the alloys tested ranged from 47.0 to 60.0 and their liquidus temperatures ranged from 2355° to 2650°F.

Threaded enlarged-end specimens were found to give more consistent values than straight rods in the tensile test. The rod portion of the threaded specimen was found to be work hardened so little by the tensile test that the same specimen can be employed for the tensile test and the determination of hardness.

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Table I

Chemical Composition of
Chromium-Cobalt Dental Alloys

Alloy	A ₁	B ₁	C ₁	D ₁	E ₂	F ₂
Cobalt %	43.5	59.4	29.7	62.6	61.5	65.0
Chromium %	21.6	30.3	22.3	26.2	27.6	30.0
Molybdenum %	7.0	5.8	3.3	5.0	5.3	4.0
Nickel %	20.1	1.5	0.7	2.3	2.3	---
Iron %	0.25	0.7	40.0	1.0	1.6	---
Silicon %	0.35	0.55	1.7	0.55	3	---
Tungsten %	---	0.35	---	1.2	---	---
Manganese %	3.0	0.34	0.9	0.16	0.8	---
Copper %	3.5	---	---	0.20	---	---
Beryllium %	0.9	---	---	---	---	---
Carbon %	0.05	N.D. ⁵	N.D. ⁵	0.25	3	---
Others %	---	---	---	---	1.0 ³	1.0 ⁴

¹ Analyzed at National Bureau of Standards.² Reported by Manufacturer.³ Reported under "Others" as total Si, C, Al.⁴ Unspecified additions.⁵ No determination.

Table 2

MECHANICAL PROPERTIES OF ALLOY A
AS CAST BY DIFFERENT LABORATORIES

Type of Specimen	Rod	Threaded		
Laboratory	Manufacturer	CDL-WR- <u>4</u>	NBS	CDL-St. L. <u>2</u>
Number of Specimens	4	10	5	11
Modulus of Elasticity				
Mean Value (psi)	32.5×10^6	32.0×10^6	28.5×10^6	25.5×10^6
$\sigma \frac{1}{\underline{2}}$ (psi)	3.0×10^6	1.0×10^6	2.5×10^6	1.5×10^6
C.V. <u>2</u> (percent)	9.0	3.0	8.5	6.5
Yield Strength				
Mean Value (psi)	$60,500$	$65,000$	$64,000$	$64,000$
σ (psi)	$8,000$	$4,500$	$5,500$	$2,500$
C.V. (percent)	13.0	7.0	8.5	4.0

Table 2 (Continued)

Type of Specimen	Rod	Threaded		
Laboratory	Manufacturer	CDL-WR ⁴	NBS	CDK-ST. L. ⁵
Number of Specimens	4	10	5	11
<u>Tensile Strength</u>				
Mean Value	(psi) 96,500	3 108,000	94,500	115,500
σ	(psi) 4,000	7,500	11,500	9,500
C.V.	(percent) 4.0	7.0	12.0	8.5
<u>Elongation</u> (1-inch gage length)				
Mean Value	(percent) 1.8	3 2.9	1.2	4.0
σ	(percent) 1.1	1.3	---	2.2
C.V.	(percent) 60.0	45.0	---	55.0

¹ Standard Deviation.
² Coefficient of Variation.
³ 2-inch gage length.
⁴ Central Dental Laboratory of Walter Reed Army Medical Center.
⁵ Fifth Army Central Dental Laboratory at Saint Louis.

Table 3

MECHANICAL PROPERTIES of ALLOY B
As Cast by Different Laboratories

Threaded Specimens

Laboratory	CDL-WR ³	Manufacturer
Number of Specimens	8	9
<u>Modulus of Elasticity</u>		
Mean Value σ^1 (psi) C. V. $\frac{1}{2}$ (percent)	31.0×10^6 1.2×10^6 3.5	28.0×10^6 2.5×10^6 9.0
<u>Yield Strength</u>		
Mean Value σ (psi) C. V. (percent)	65,500 4,500 7.0	57,000 3,500 6.0
<u>Tensile Strength</u>		
Mean Value σ (psi) C. V. (percent)	117,500 9,500 8.0	98,000 6,000 6.0
<u>Elongation</u> (1-inch gage length)		
Mean Value σ (percent) C. V. (percent)	1.2 0.2 18.0	4.3 1.7 40.0

1 Standard Deviation,

2 Coefficient of Variation.

3 Central Dental Laboratory, Walter Reed Army Medical Center.

Table 4

MECHANICAL PROPERTIES OF CHROMIUM-COBALT DENTAL ALLOYS
AVERAGE OF ALL THREADED SPECIMENS

Alloy	A	B	C
Number of Specimens	26	17	6
<u>Modulus of Elasticity</u>			
Mean Value (psi)	28.0×10^6	29.5×10^6	26.0×10^6
σ ¹ (psi)	2.0×10^6	2.5×10^6	1.5×10^6
C. V. ² (percent)	7.0	8.0	6.5
<u>Yield Strength</u>			
Mean Value (psi)	64,500	61,000	49,500
σ (psi)	4,500	7,000	8,000
C. V. (percent)	7.0	11.5	16.5
<u>Tensile Strength</u>			
Mean Value (psi)	108,500	107,500	104,000
σ (psi)	12,000	12,500	8,500
C. V. (percent)	11.0	11.5	8.0
<u>Elongation</u> (1-inch gage length)			
Mean Value (percent)	3.4	3.2	2.7
σ (percent)	1.9	2.1	1.5
C. V. (percent)	55.0	65.0	56.0

1 Standard Deviation.

2 Coefficient of Variation.

Table 4 (Continued)

Alloy	D	E	F
Number of Specimens	5	18	9
<u>Modulus of Elasticity</u>			
Mean Value (psi)	27.5×10^6	28.5×10^6	29.0×10^6
σ ¹ (psi)	2.5×10^6	3.5×10^6	1.0×10^6
C. V. ² (percent)	9.5	12.0	4.0
<u>Yield Strength</u>			
Mean Value (psi)	56,000	62,400	60,000+ ³
σ (psi)	4,000	3,000	-----
C. V. (percent)	7.0	5.0	-----
<u>Tensile Strength</u>			
Mean Value (psi)	84,500	102,500	105,100
σ (psi)	4,000	10,000	6,500
C. V. (percent)	5.0	10.0	6.0
<u>Elongation</u> (1-inch gage length)			
Mean Value (percent)	6.0	1.9	1.9
σ (percent)	2.9	0.8	0.9
C. V. (percent)	48.0	40.0	47.0

3 Minimum value determined in accordance with proposed specification.

Table 4 (Continued)

Alloy	No. of Specs.	Hardness (R 30N)		
		Mean Value	σ	C. V. (percent)
<u>A</u>	26			
a		53.0	2.0	4.0
b		47.0	4.5	9.5
<u>B</u>	17			
a		60.0	1.0	2.0
b		57.0	1.5	2.5
<u>C</u>	6			
a		54.0	1.5	3.0
b		49.0	1.0	2.0
<u>D</u>	5			
a		51.0	1.0	2.0
b		49.0	1.5	3.0
<u>E</u>	18			
a		55.0	0.5	1.0
b		51.0	1.0	2.0
<u>F</u>	9			
a		58.0	1.5	2.5

a Rod portion.

b Threaded portion.

Table 5

EFFECT OF PRIOR TENSILE TESTING ON HARDNESS

Alloy	As Cast		After Tensile Test	
	Rod Portion	Threaded Portion	Rod Portion	Threaded Portion
A	53.0	47.0	54.0	52.0
B	60.0	57.0	60.0	60.0
C	54.0	49.0	50.0	48.0
E	55.0	51.0	54.0	53.0

All values are average Rockwell 30N hardness.

Table 6

Liquidus Temperature of
Chromium-Cobalt Dental Alloys

Alloy	Liquidus °F
A	2355
B	2605
D	2575
E	2650 ¹
F	2560

1 As reported by manufacturer.

TENSILE TEST SPECIMEN

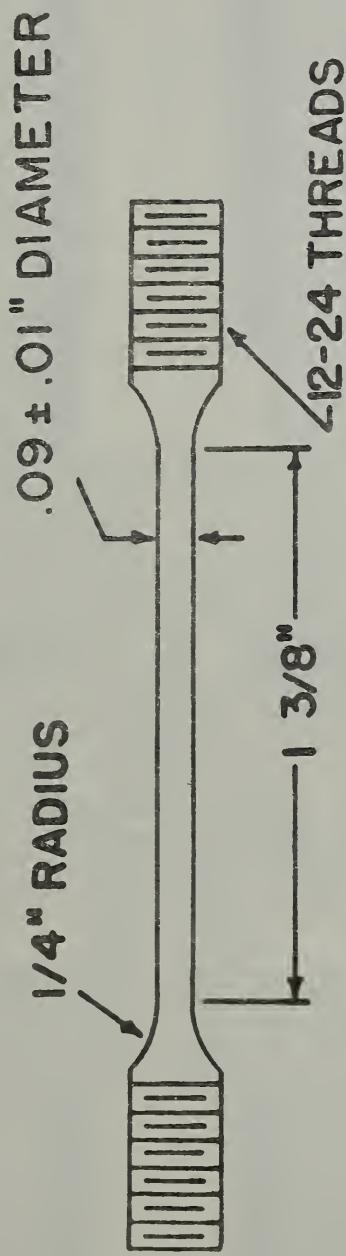


Figure 1. Specimen design for tensile test

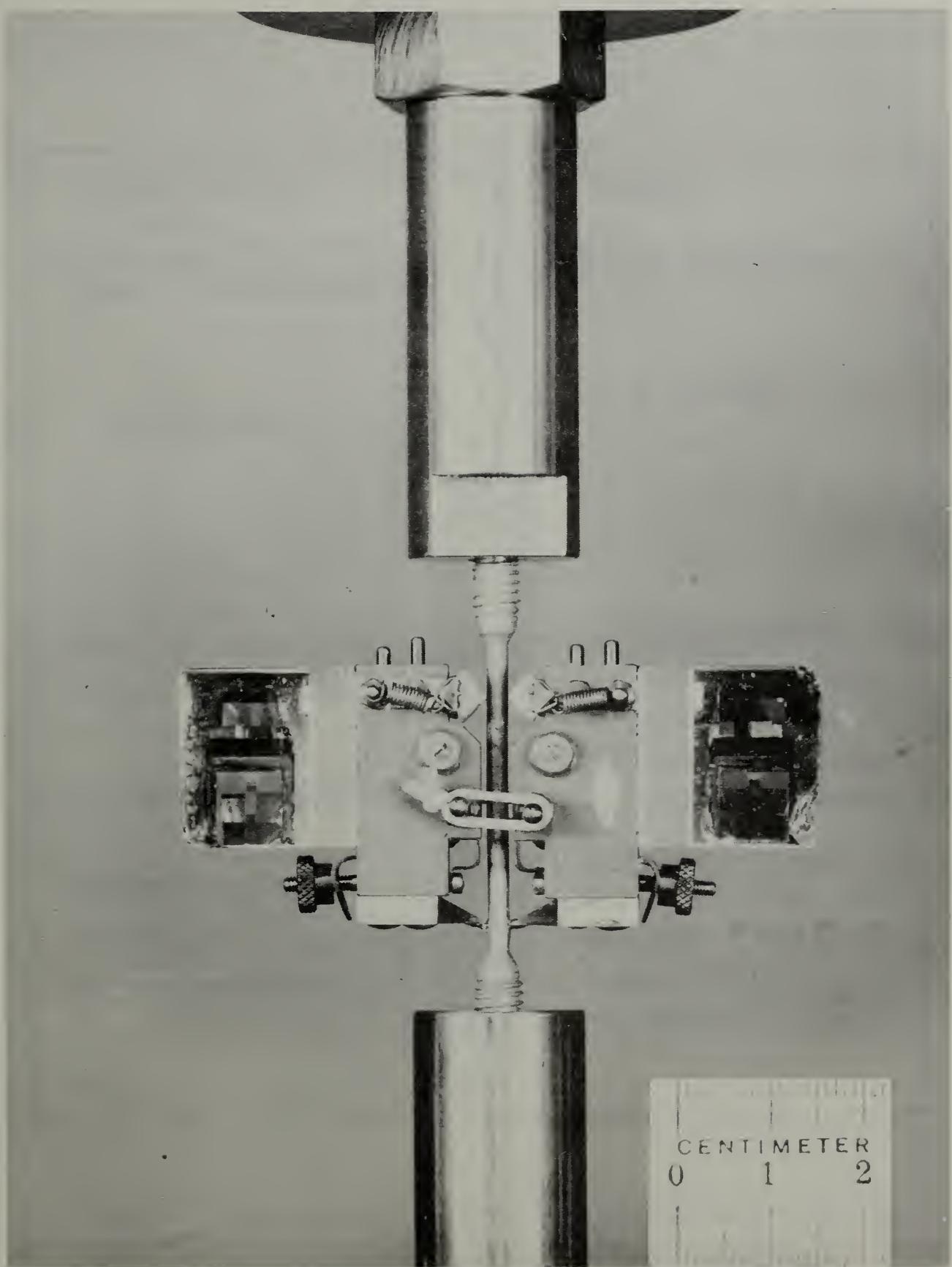


Figure 2. Tensile specimen in testing machine grips
showing mounting of strain gages.

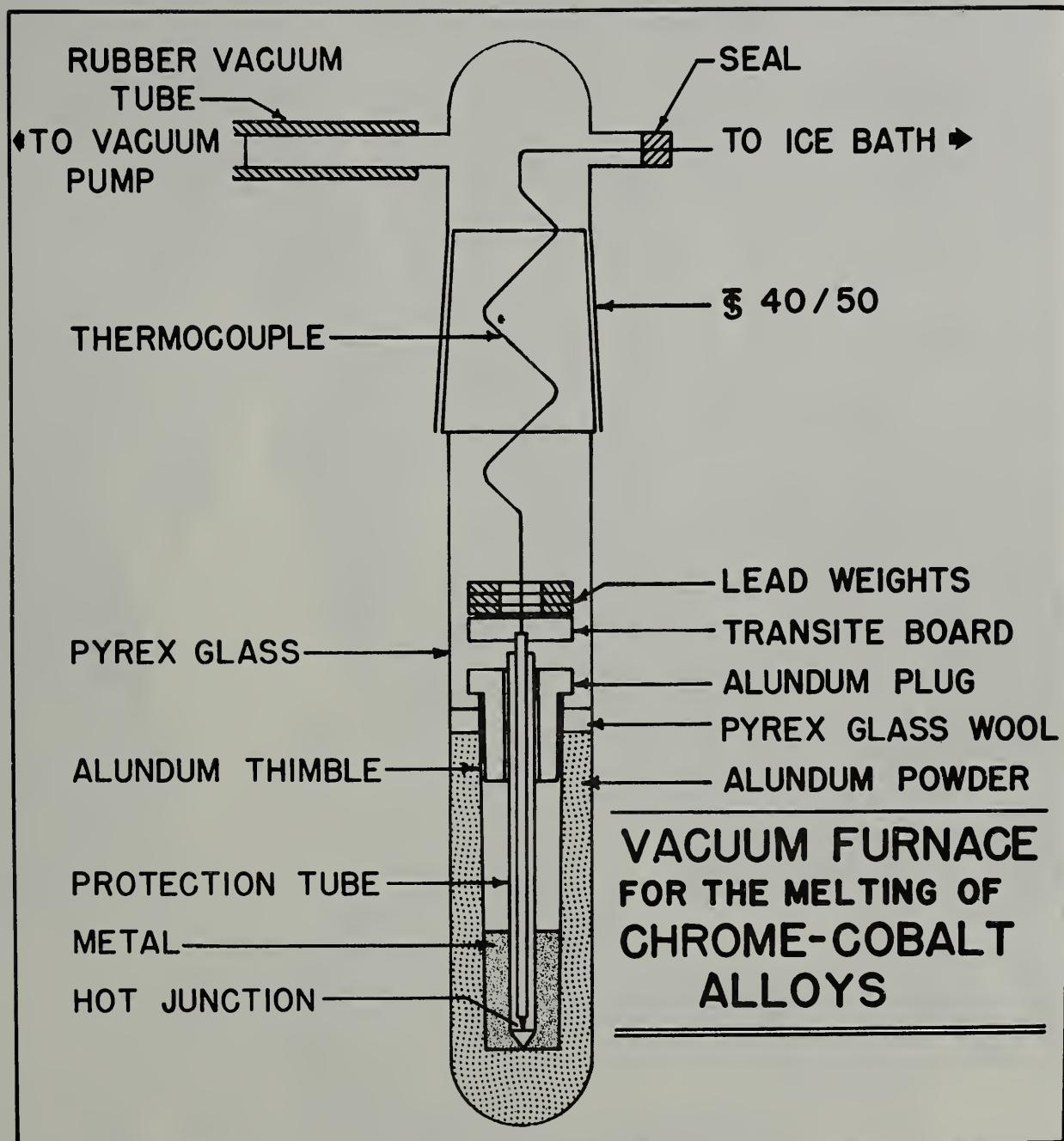


Figure 3. Schematic drawing of vacuum furnace for the induction melting of small specimens.

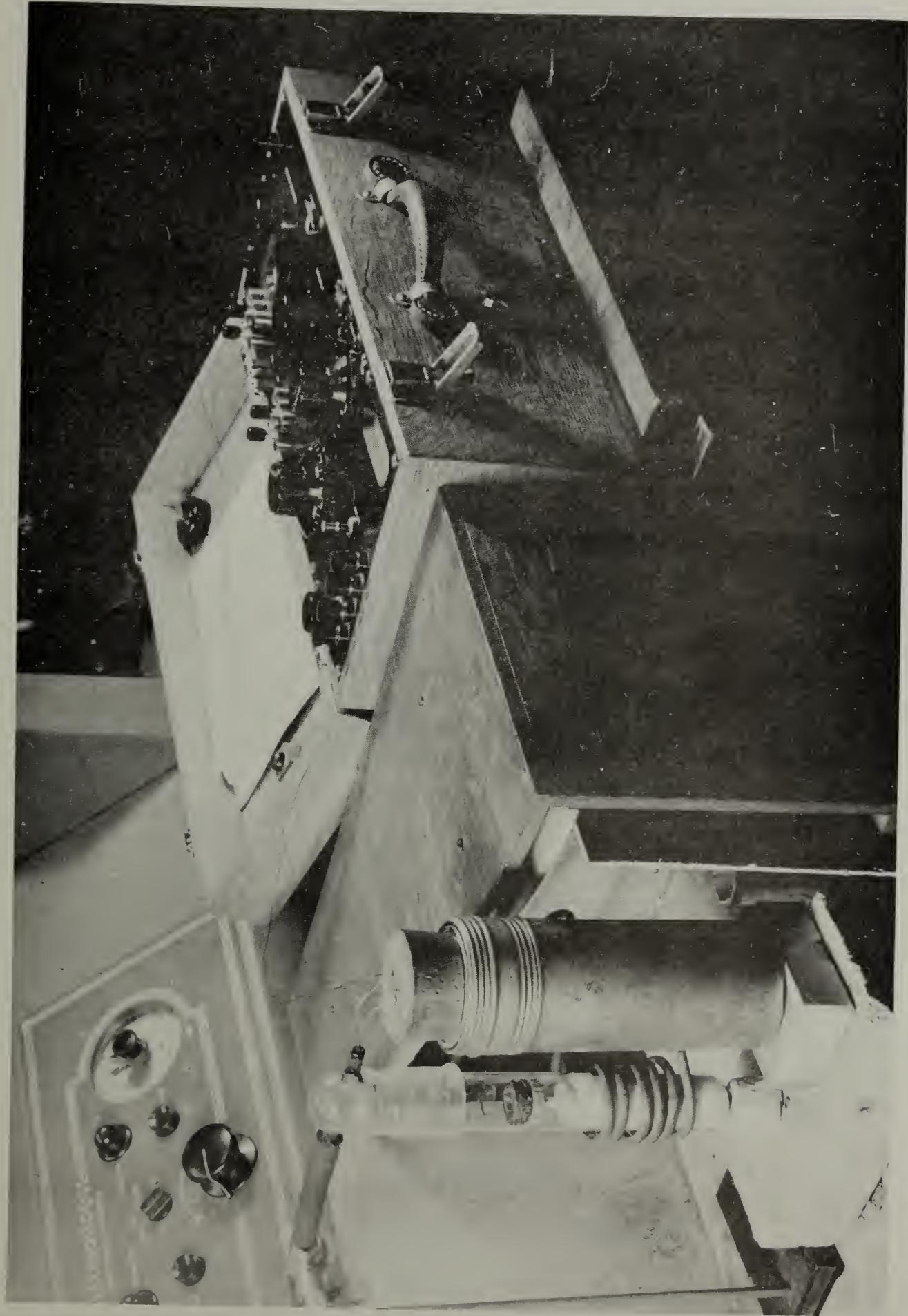


Figure 4. Apparatus employed for liquidus temperature determinations.

TYPICAL STRESS STRAIN CURVE

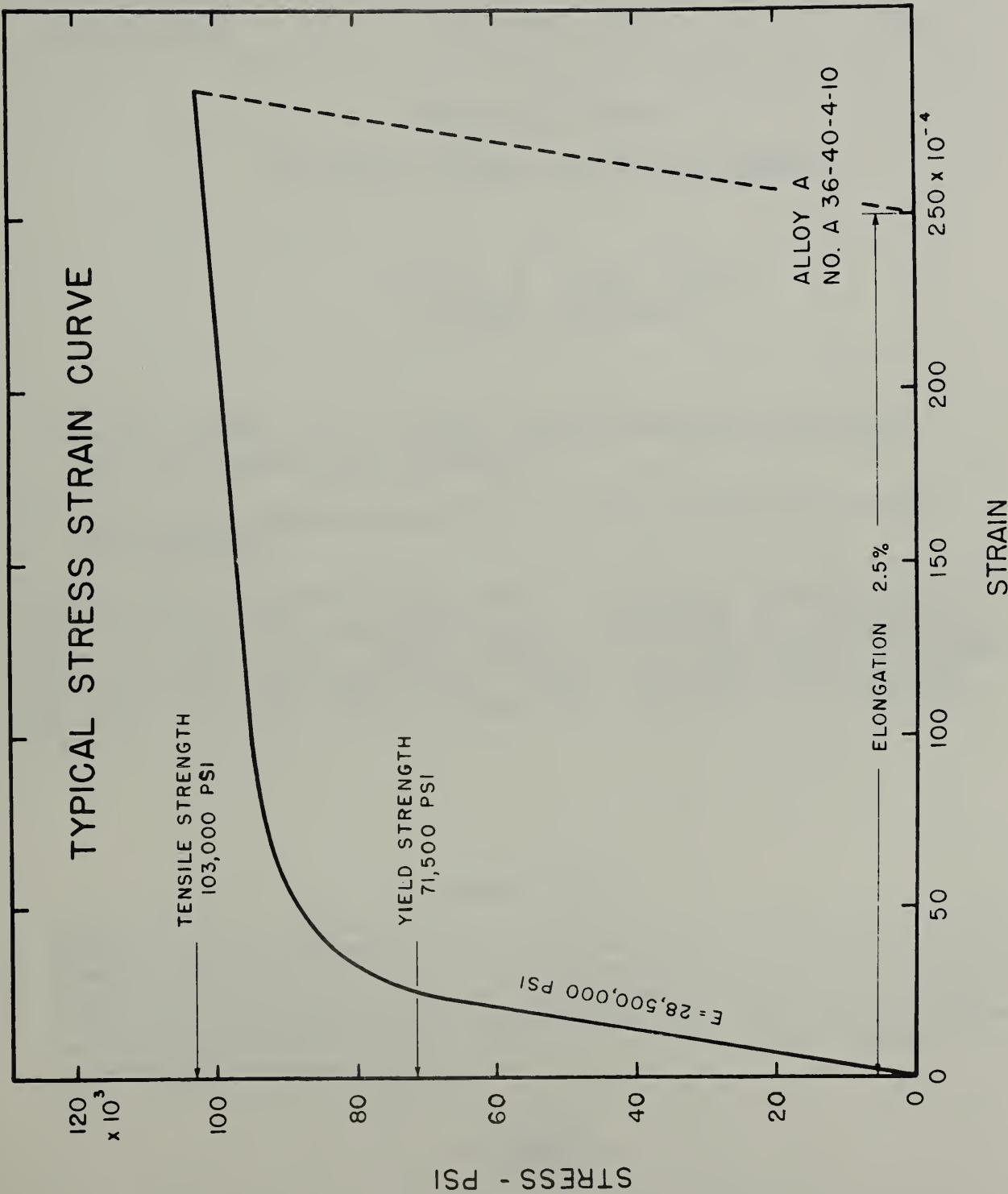


Figure 5. Stress-strain curve for typical tensile specimen.

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COLORS OF DENTAL SILICATE CEMENTS

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U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

COLORS OF DENTAL SILICATE CEMENTS

Abstract

The colors of dental materials are of major importance to the dental profession. In this study the colors of 30 shades of silicate cements were measured, their color change with time was observed and the differences in color with different powder-liquid ratios were also measured. The colors were plotted on the x,y-chromaticity diagram located between the white and yellow areas. The data indicate that development of a system of shade designations based on tristimulus values Y and Z may be possible. The color change showed a darkening of the specimen which would be barely discernable to the human eye. Different powder-liquid ratios within normal usage ranges showed no significant color differences.

1. INTRODUCTION

Although many of the physical properties of dental materials have been extensively studied, very little work has been done to apply scientific color measurement to these materials [1]. The color is probably the most important property in the selection of silicate cement for restoration of teeth in the

anterior position of the mouth because of the necessity for producing an aesthetically acceptable reproduction of the natural tooth. Several methods of color designation have been devised [2, 3] and a number of systems for measuring color [2, 3, and 4] have been developed. Several of the standard color specification methods were studied for use with silicate cements in an effort to place the colors of dental materials on a scientific basis so that their colors may be standardized.

Dental silicate cements, used as a filling material for anterior teeth, are manufactured in a wide range of shades by the several dental manufacturing companies. However, the method of shade designation was developed independently by each individual company and since this is true, there is no uniform system of shade designation. This is of special concern to the Armed Services, since a shade ordered by name may not be the same color if two samples were supplied by different companies.

In this study, which was undertaken to provide some basic data on silicate cement colors, the colors of several hundred samples of silicate cements were measured, their change of color with time was observed, and the differences in color with different powder-liquid ratios were determined.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

Silicate cements, as purchased by the dentist, consist of a dry, pulverized glass composed mainly of silica and alumina

and a liquid which is essentially diluted, buffered, phosphoric acid. These two substances are mixed into a plastic mass in definite ratios and allowed to set into a rigid gel [5]. Standard shades sold by the L. D. Caulk Company and the S. S. White Dental Manufacturing Company were used in this investigation.

2.2 Mixing and Molding

Samples were prepared by weighing enough powder on a torsion balance to mix with 0.6 ml of liquid, dispensed from a 2.0 ml capacity syringe, to form a mass of the standard consistency [6]. The powder and liquid were spatulated for one minute on a glass slab. After mixing, the plastic mass was placed in a special stainless steel mold and discs, 3/4" in diameter and 1/8" thick were pressed between glass plates. Preliminary study had shown that a specimen thickness of at least 1/8" should be used to minimize the error caused by the transmission of light through thinner specimens.

The specimens in the molds were immediately placed in a container at 100% relative humidity for one hour. The discs were then removed from the molds and the color measured. After the initial measurement, the samples were stored in distilled water.

2.3 Color Measurement

All measurements were made with the Gardner Automatic Color Difference Meter (Figure 1). This is an improved model of the manually operated Hunter tristimulus colorimeter. In the auto-

matic instrument the light from a tungsten source is divided into 2 parts by an optical system and focused to strike the sample at a 45° angle of incidence in a small spot about $3/8$ inch in diameter. The light is perpendicularly diffused from the sample and through a system of three filters and photo-cells, transformed into electric currents, which are sent to the measuring unit. The currents are passed through an electronic circuit connected to motor-driven dials mounted on the front of the instrument. These dial readings will then give a complete colorimetric specification of the sample.

The silicate cement discs must be kept moist at all times to avoid "chalking," therefore a special cell was constructed so that the samples could be immersed in distilled water for all measurements. This cell had a bottom of boro-silicate optical glass. The cell is shown in position on the instrument in Figure 1. The samples were placed in the cell and covered with water to a depth of about $1/2$ inch. The color was then measured.

The instrument gives the colorimetric description as three values, " R_d ," "a," and "b." R_d is defined [7] as 100 times the amount of light reflected by a sample divided by the amount of light reflected by a perfectly diffusing sample (actually by MgO), when the light is incident upon the sample at an angle of 45° and the measuring device indicates the light diffused perpendicularly from the sample.

A black, completely absorbing sample would have an R_d value of zero while a pure white, perfectly diffusing specimen, would have a value of 100. "a" and "b" are [7] the rectangular coordinates of color in any plane intersecting the color-solid perpendicularly to the black-white axis. Zero values of "a" and "b" indicate that the color of the sample is on the black-white axis, or some shade of gray, when "a" has a positive value, the color is on the red side while a negative value places it on the green side. Similarly, a positive value of "b" indicates that the color is in the yellow region and a negative value shows that it contains blue.

Previously calibrated samples of porcelain-enamel were used as a primary standard and small porcelain chips with spectral characteristics similar to those of each shade were used as secondary standards.

Several of the universally accepted methods of color designation can be calculated from the " R_d ," "a," "b" values. The tristimulus coordinates X, Y and Z are related to " R_d ," "a," and "b" as indicated by the following equations [7]

$$R_d = 100 Y \quad (1)$$

$$a = (175) (0.51 \frac{21 + 20Y}{1 + 20Y}) (1.02X - Y) \quad (2)$$

$$b = 70(0.51 \frac{21 + 20Y}{1 + 20Y}) (Y - 0.847 Z) \quad (3)$$

The tristimulus coordinates, which are the representations of the primary colors required to produce for the standard observer the color at any wave length, are used to calculate

the chromaticity coordinates, x, y and z. These are the tri-stimulus values expressed as a fraction of their total, or

$$x = \frac{X}{X + Y + Z} \quad (4)$$

$$y = \frac{Y}{X + Y + Z} \quad (5)$$

$$z = \frac{Z}{X + Y + Z} \quad (6)$$

If the x coordinate is plotted against the y value for the spectral colors, a graph as shown in Figure 2 is obtained. The coordinates for the spectrum loci are shown by the curve itself, while mixtures of colors are located within the enclosed area.

The National Bureau of Standards unit of color difference was used in this study for showing color change with time. This designation of color difference, given the symbol ΔE , is a vectoral sum of the component differences as

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2} \quad (7)$$

where

$$L = 10 \sqrt{R_d} \quad (8)$$

3. RESULTS AND DISCUSSION

The chromaticity coordinates for 30 shades of silicate cements were determined and plotted (Figure 3) the range of color of the cements lies between white and yellow areas of the diagram with small amounts of red or green added. The

location in relation to the principal colors can be seen since R indicates the red area, Y the yellow, G green, and B blue. If the portion of the diagram containing the silicate cement colors is greatly expanded (Figure 4), a more accurate representation of the relationship between shades is seen. The distribution of shades throughout the whole area is fairly uniform, although it seems that a good many shades could be eliminated without seriously affecting the colors available to the dentist.

Another factor that is important is the change of color with time. Here, the NBS unit of color difference is used as the basis of comparison. The size of this unit can be visualized from the knowledge that one unit is usually disregarded in commercial transactions, a difference of two units is considered a match in wool dyings and a difference of four units in cotton dyings [3]. The color of a typical cement will change from 4 to 6 NBS units (Figure 5) during the period from mixing until a stable color is obtained. This equilibrium color was reached in about 2 to 3 weeks after mixing. Similar shades from different manufacturers had approximately the same change of color (Figure 6).

This color change is mostly due to a darkening of the sample (Figure 7). If "R," "a," and "b" are plotted on the same scale, which can be done since their units are approximately the same size, it can be seen that the reflectance, or lightness, has the largest change, "b" or yellow changes only

slightly while "a" or green has no significant change. This difference in R_d is probably due to a change in opacity, rather than actual pigmentation. As silicates age, they become less opaque and more translucent. Since the R_d value is based upon reflected light, a more translucent sample would transmit more of the incident light than previously, reflecting less and giving a lower R_d value.

Since varying amounts of powder would have slightly different quantities of pigment, a study was made to see if this would have a significant effect on the color, as a difference in powder-liquid ratio does affect the other properties of the cement [8]. Several samples with different powder-liquid ratios were mixed and their colors measured. The color differences of these samples when compared to those mixed to a standard consistency (1.50 g of powder to 0.4 milliters of liquid) are shown in Figure 8. The change in the ratio has very little effect upon the color, except at very low powder quantities. A ratio of 1.25/0.4 gives a very light sample with a difference of several units, but the samples were not uniform in color and since they had a very thin mix, probably would not be used by the dentist. The results from this investigation clearly show the need for a shade requirement in specifications for silicate cements. Although the range of manufactured shades probably covers the range of natural tooth colors, there appears to be an excess of shades in certain regions of the chromaticity

diagram. A study of the tristimulus values X, Y and Z for the 30 shades of cement included in the present investigation indicates that a system in which Y and Z are specified might be satisfactory for designating the shades of silicate cements. In Figure 9 where Y is plotted against X it can be seen that for any given value of Y very little variation in X was observed. The plot of Y against Z, Figure 10, however, shows that these two tristimulus values did vary independently. As shown by equations 1 and 3, Figure 10 can be considered to be a representation of reflectance (Y) and yellowness (Z). The large open blocks in Figure 9 represent a possible selection of regularly spaced standard shades which cover the range observed in the present investigation. The shaded blocks can be designated numerically as shown in Table 1. Until additional studies are made this particular selection of shades cannot be recommended as the most satisfactory choice. Also additional information is needed on the tolerances which are necessary on shade designations. These tolerances will depend upon the practical limits of color control in the manufacturing of silicate cements and upon the reproducibility of color measurements made in different laboratories.

4. SUMMARY

When the colors of dental silicate cements are plotted on the x,y-chromaticity diagram, the shades lie between the white and yellow regions of the graph, with small amounts of red or

green added. By inspection of an expanded diagram it seems that an excess of shades are provided in some areas of the diagram and that several shades could be eliminated without affecting the dentists' ability to match anterior tooth color. A study of the data obtained indicate that a system of standard shades based on the specification of the tristimulus values for Y (reflectance) and Z (yellowness) could be developed.

A color change of an amount discernable to the human eye occurs during a two to three week period immediately after mixing. This color change, due mostly to a darkening of the specimen, is probably caused by a decrease in opacity rather than a change in pigmentation.

Differences in powder-liquid ratio show no significant differences in color, except in cases where the quantities of powder are very low.

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Table 1. Y and Z Tristimulus Designation
of a Series of Regularly Spaced
Shades for Silicate Cements.

Y	Z			
0.18	0.14	0.17	-----	
0.21	0.14	0.17	0.20	-----
0.24	0.17	0.20	0.23	-----
0.27	0.20	0.23	0.26	-----
0.30	0.23	0.26	0.29	0.32
0.33	0.26	0.29	0.32	0.35
0.36	0.32	0.35	-----	

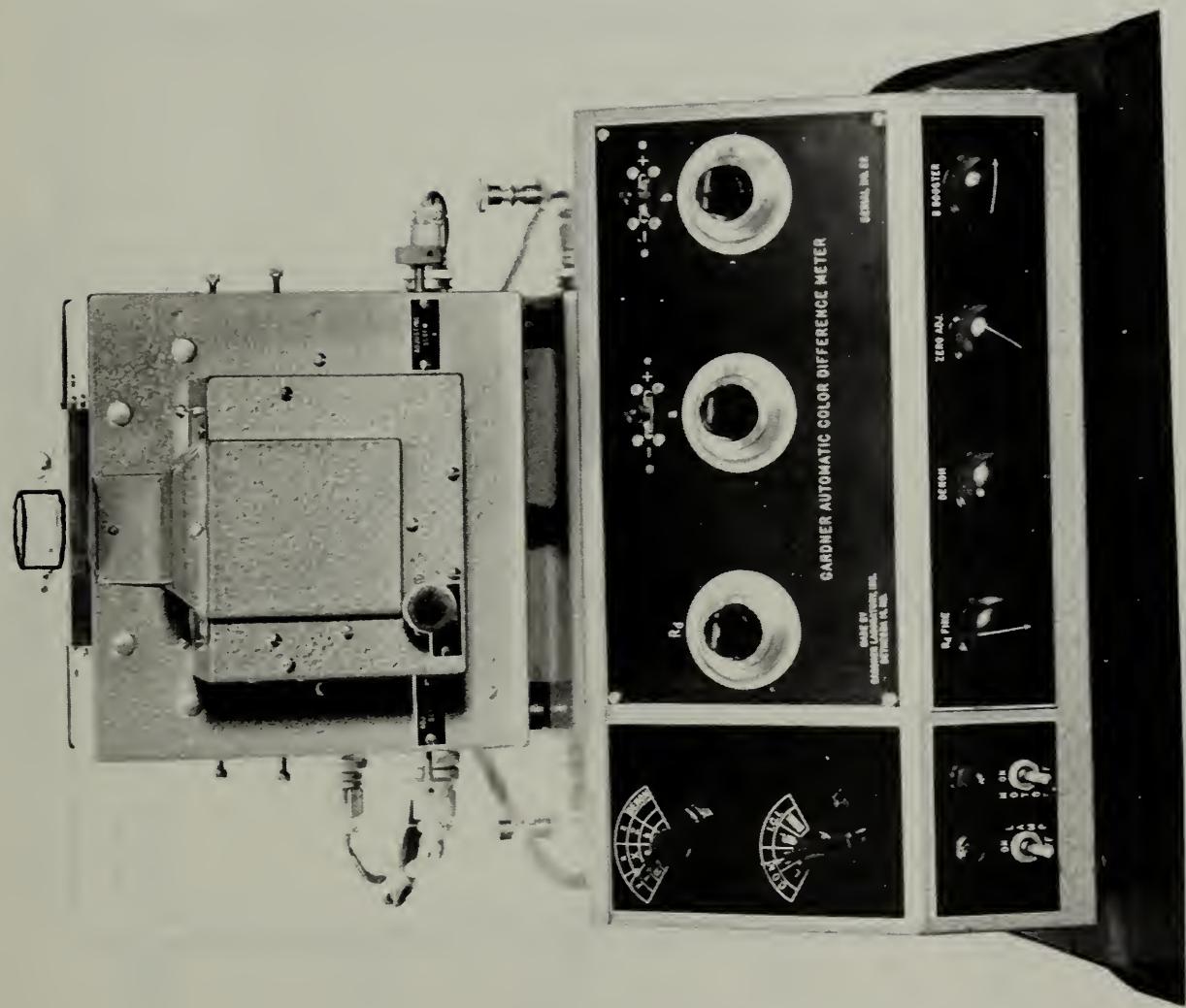


Figure 1. Gardner Automatic Color Difference Meter with specimen cell in position on top of instrument.

(x, y)-CHROMATICITY DIAGRAM

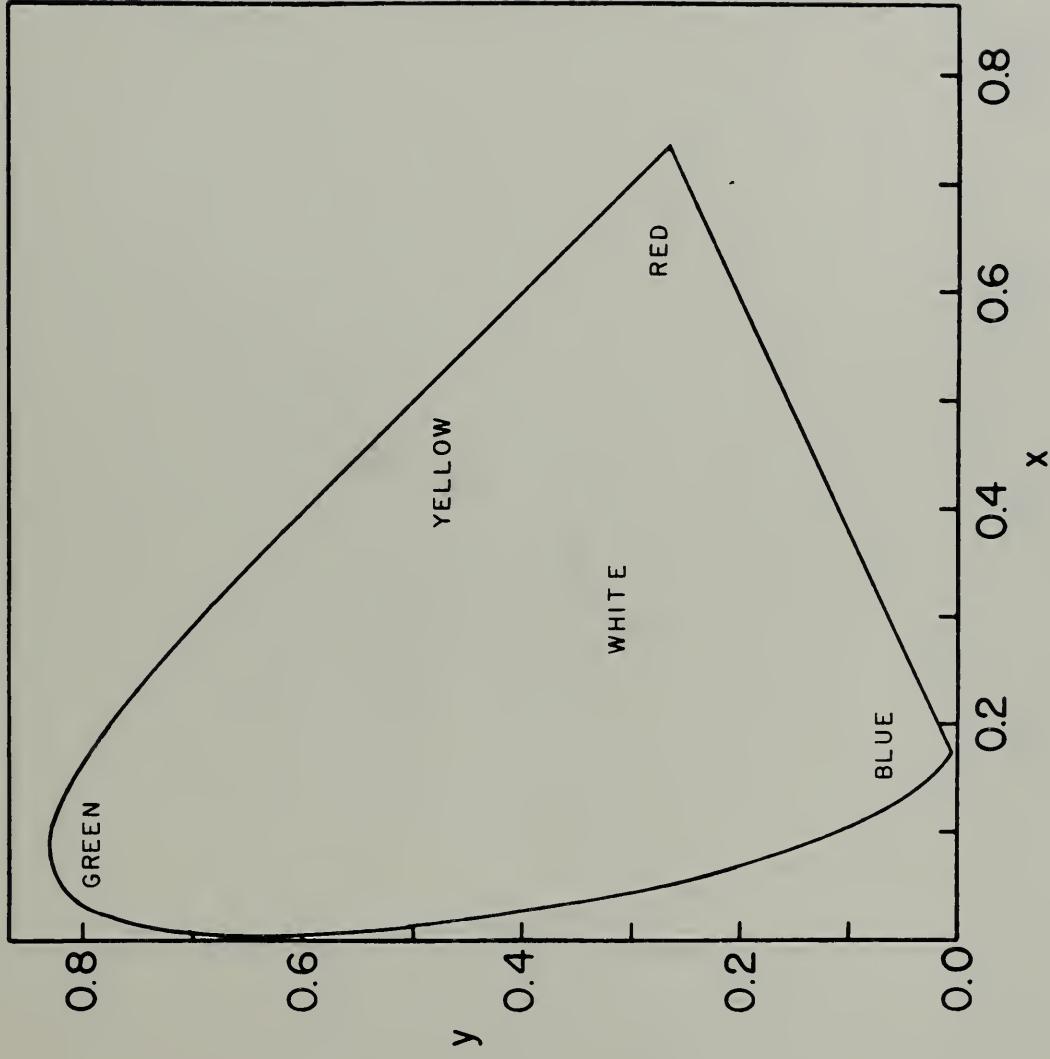


Figure 2. (x, y)-chromaticity diagram giving principal color locations.

(x,y)-CHROMATICITY DIAGRAM

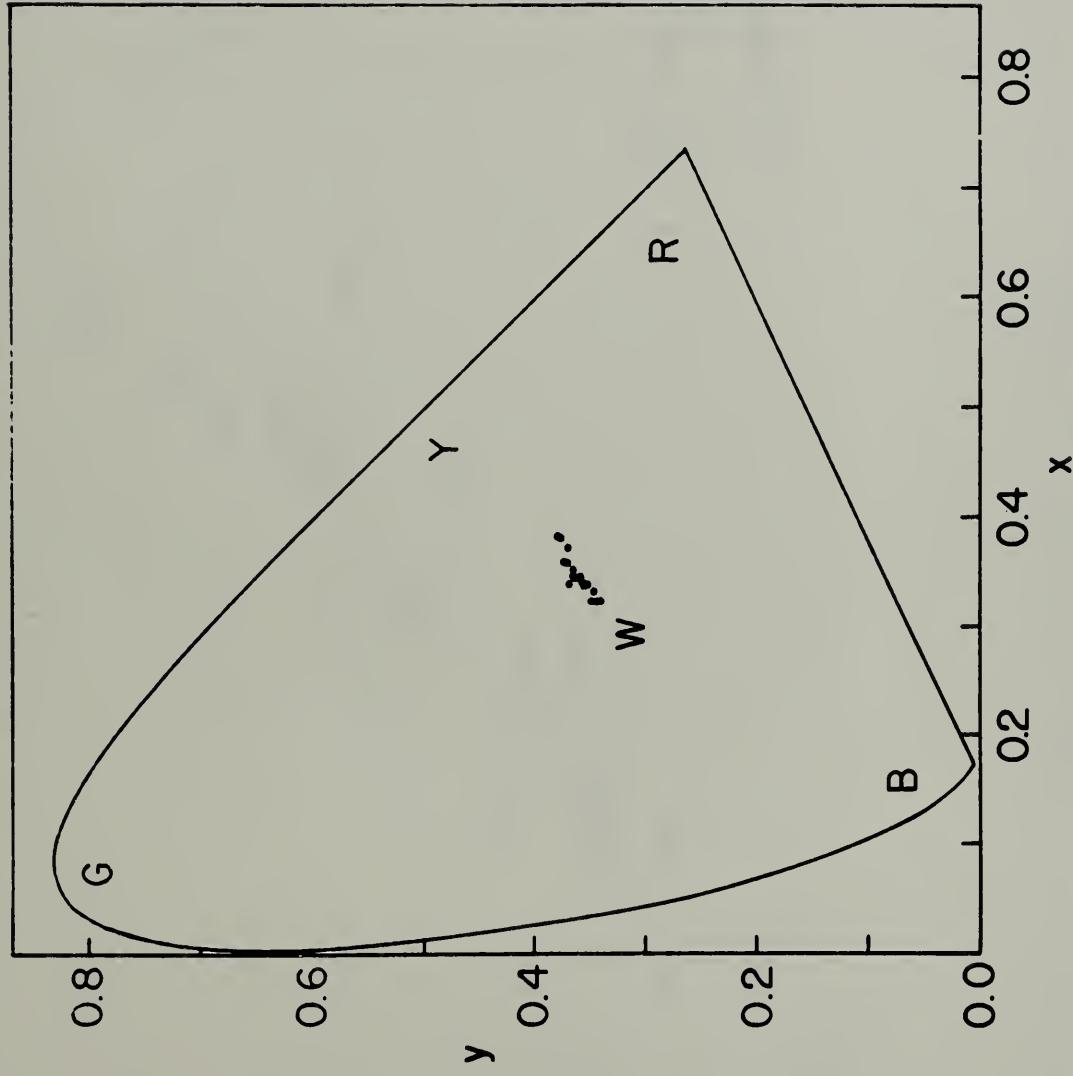


Figure 3. (x, y)-chromaticity diagram showing the plotted chromaticity co-ordinates of 30 shades of silicate cement.

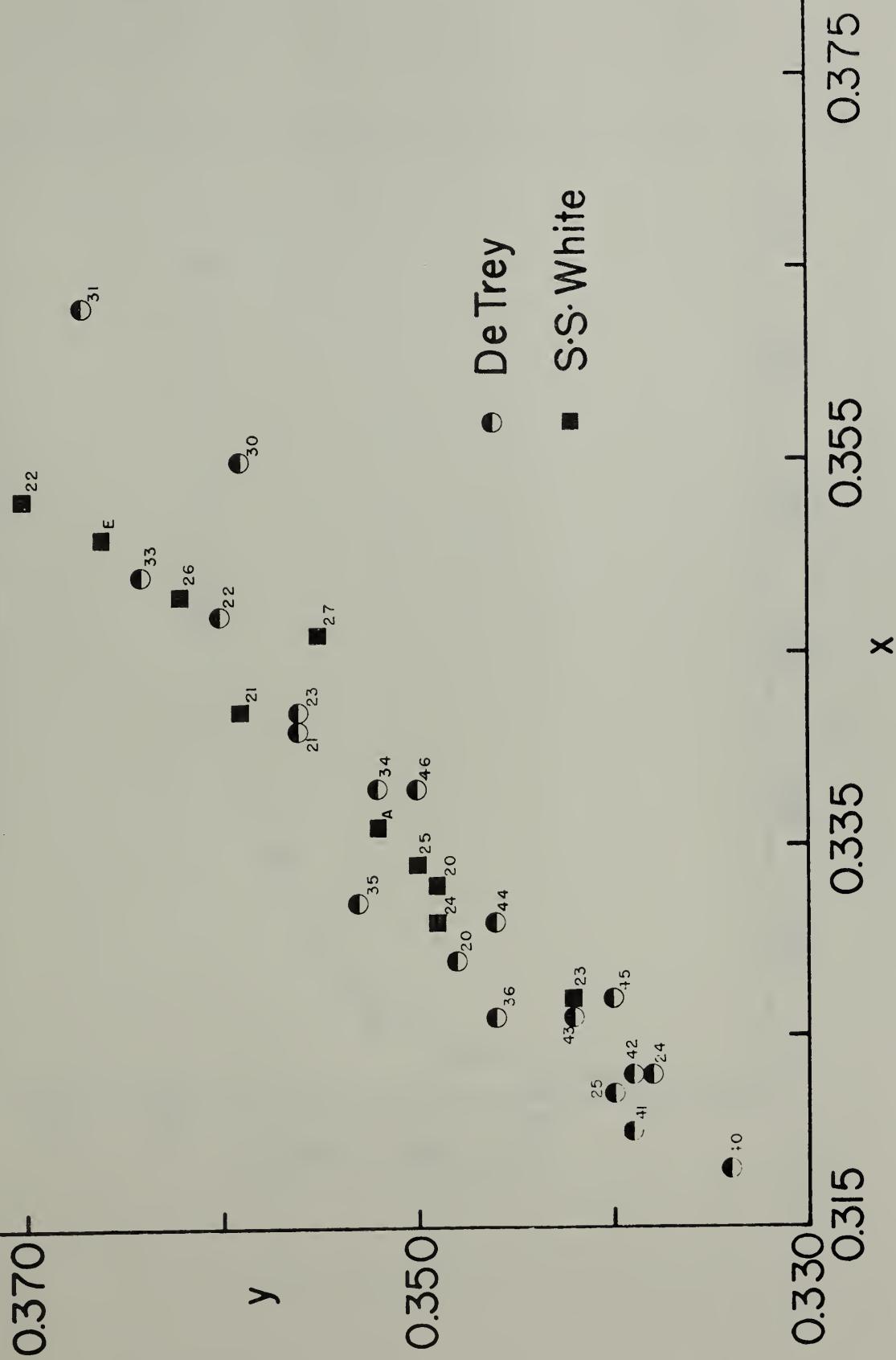


Figure 4. Expanded area of (x, y) -chromaticity diagram showing the color distribution and comparing co-ordinates of two brands of silicate cement.

Figure 4.

TYPICAL SILICATE CEMENT COLOR CHANGE

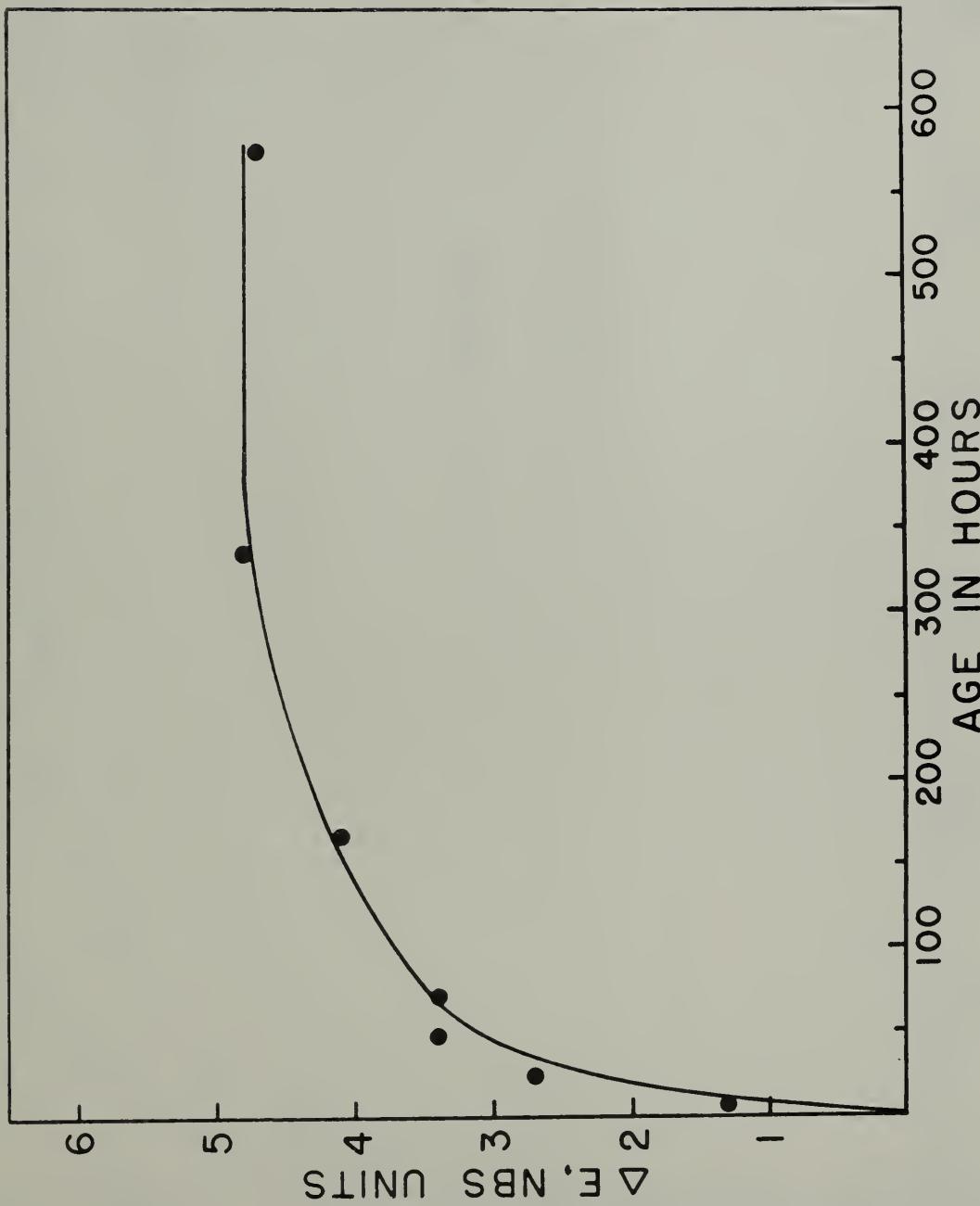


Figure 5. Color change of a typical silicate cement.

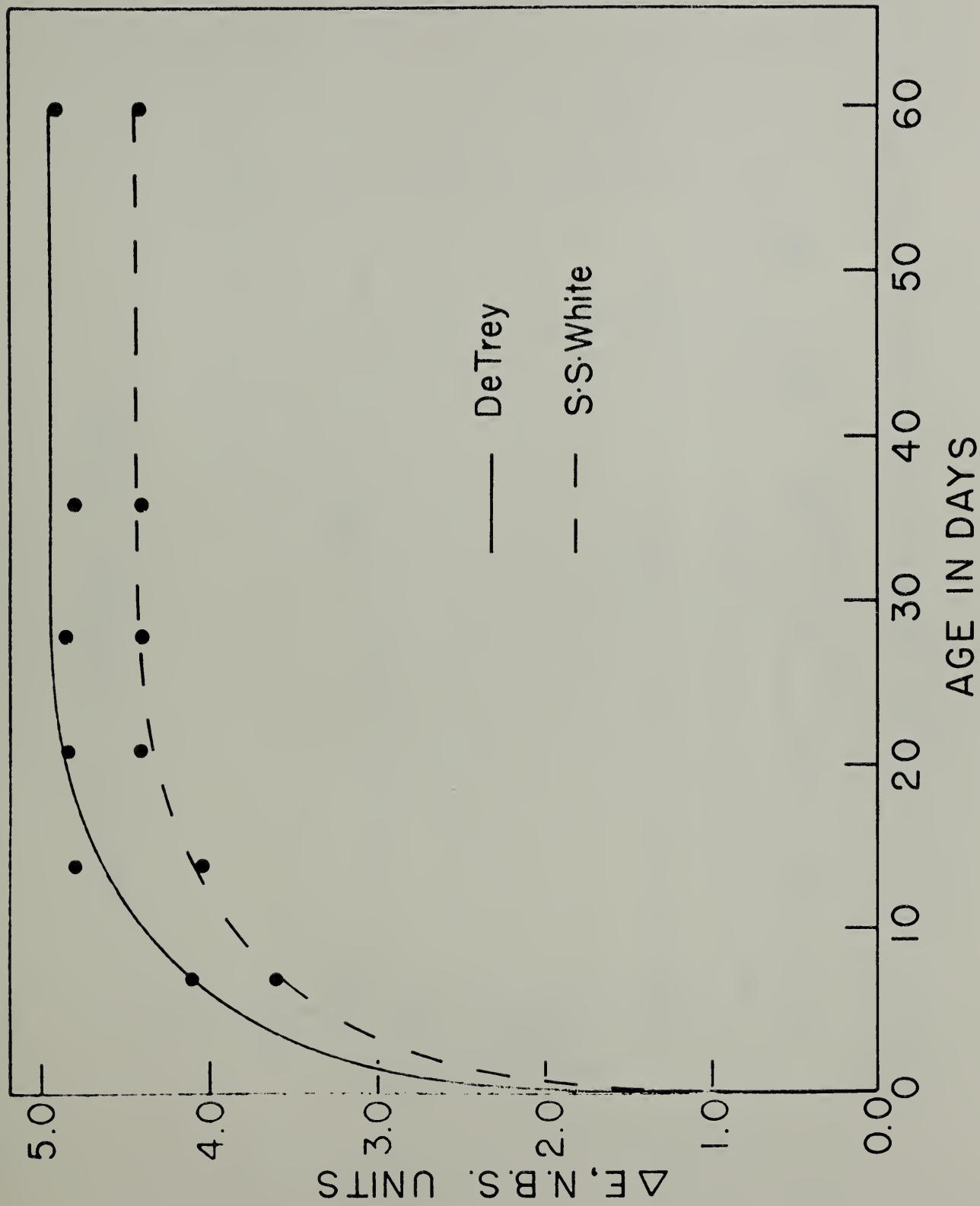


Figure 6. Comparison of color change for two brands of silicate cement.

INDIVIDUAL COMPONENT CHANGE

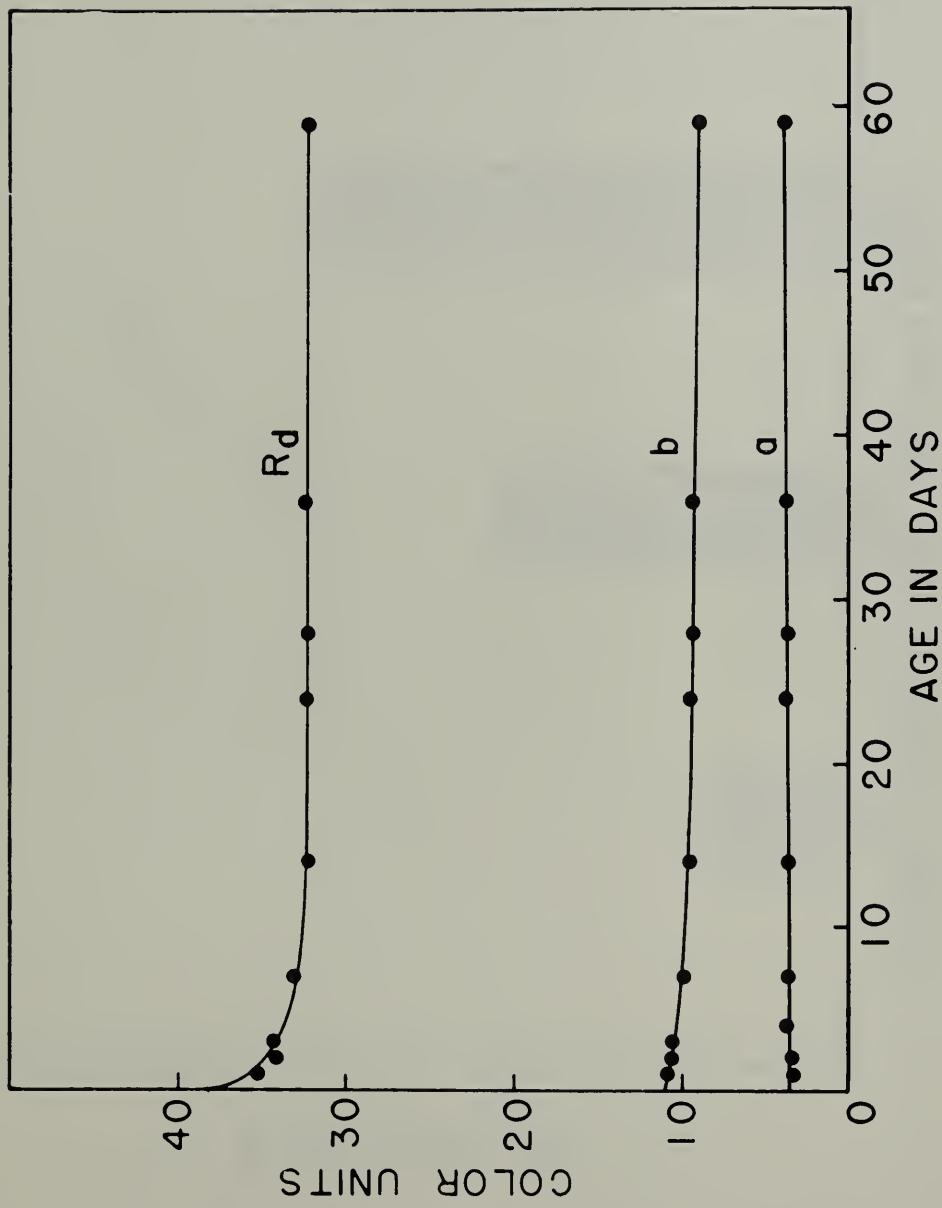


Figure 7. Individual color component color change of silicate cement in Figure 5.

POWDER-LIQUID RATIO DIFFERENCES



Figure 8. Color differences of different powder-liquid ratios compared to a standard consistency ratio of 1.50/0.4.

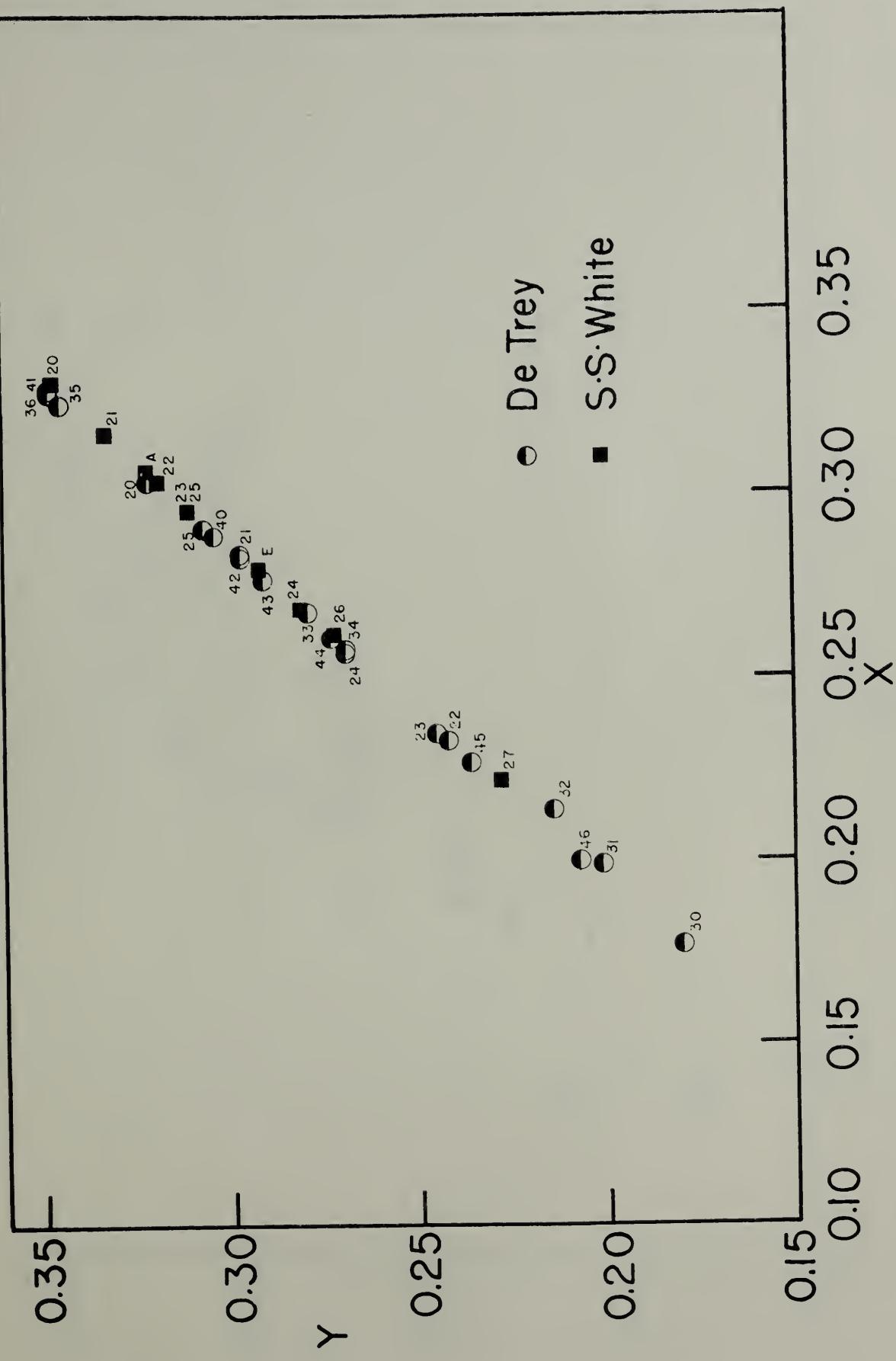


Figure 9. Tristimulus values Y and X for 30 shades of silicate cements.

Figure 9.

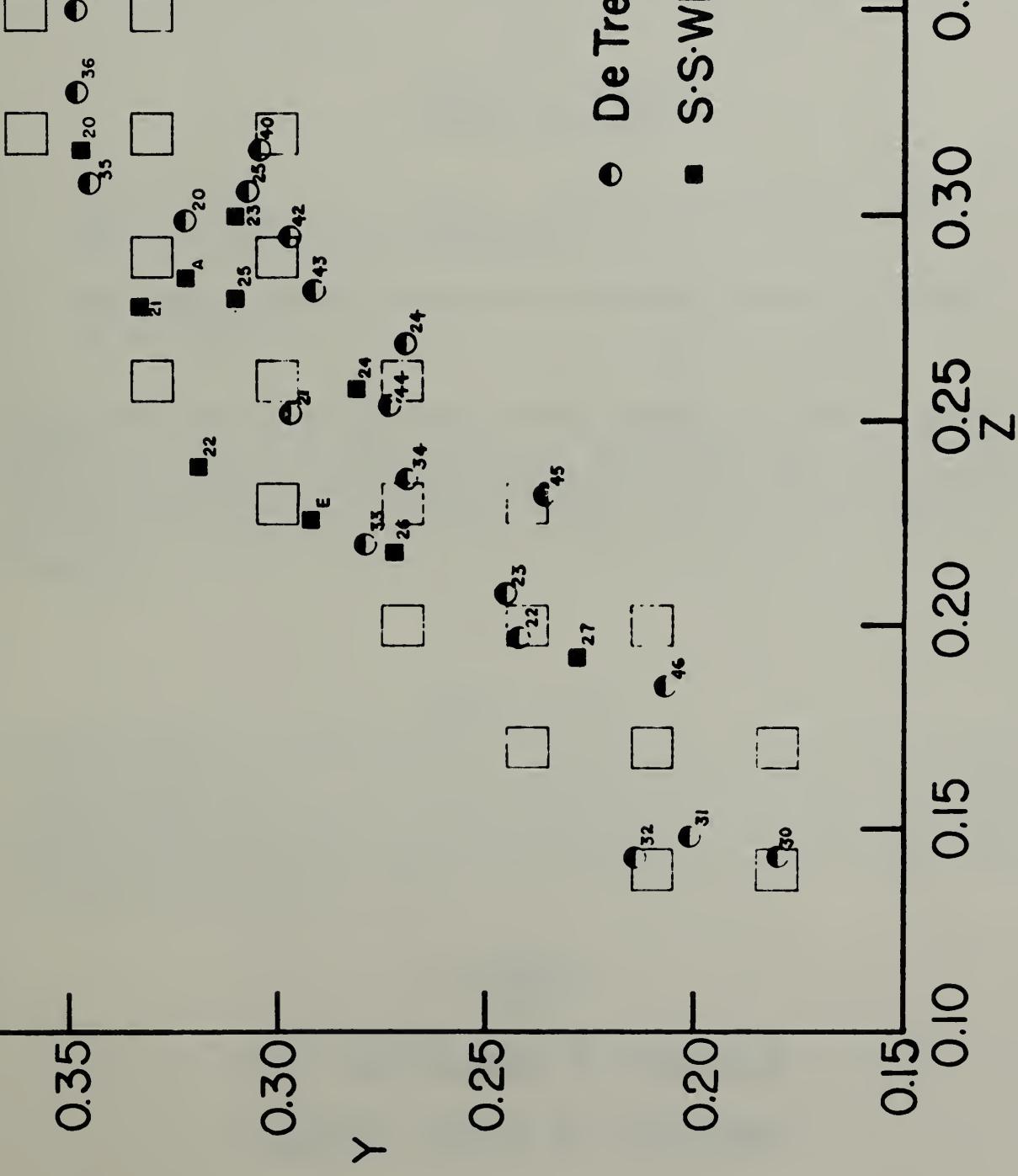


Figure 10. Tristimulus values Y and Z for 30 shades of silicate cement. The open squares show one possible selection of regularly spaced standard shades.

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MECHANICAL MIXING OF DENTAL CEMENTS

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U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

MECHANICAL MIXING OF DENTAL CEMENTS

Abstract

The effects of mechanical mixing technics on zinc oxide-eugenol and on silicate cements using a gelatin capsule as the mixing container and mixing in the Crescent Wig-l-Bug amalgamator have been investigated. Incorporation of the ingredients was achieved within seven seconds with mechanical mixing.

The zinc oxide-eugenol cements showed little change in physical properties when they were mixed by mechanical means as compared to those mixed by spatula.

The silicate cements mixed mechanically at room temperature had slightly decreased setting times and had compressive strengths not significantly different from spatula-mixed specimens. Specimens mixed mechanically at reduced temperatures had similar setting times and similar or lower compressive strengths than those of the spatula-mixed specimens. In general, the silicate cements mixed mechanically exhibited an increase in solubility and disintegration compared to those which were mixed by spatula. Variations were found to exist between different brands of silicate cement.

1. INTRODUCTION

It is well known that the properties of the dental cements depend to a considerable extent upon the method of mixing the

cement powder and liquid. This is especially true with the silicate cements, and recently several methods have been suggested as possible means of improving their physical properties [1, 2].

It was thought that mechanically mixing the dental cements might offer certain advantages over the usual method of mixing these cements with a spatula on a glass slab. Specifically it was thought that mechanical mixing might achieve:

1. Increased efficiency through reduced mixing time and elimination of the necessity of cleaning the mixing equipment.
2. A more standardized mix and technic.
3. Physical and chemical properties equal or superior to those produced by hand spatula mixing.

2. EXPERIMENTAL PROCEDURE

2.1 Mixing Technic

Of the various methods studied the Crescent Wig-l-Bug amalgamator appeared to offer the most convenient method of mixing or incorporating the ingredients. A study of possible usable mixing containers indicated that the number 000 gelatin capsule was the most convenient for use in mechanical mixing. Glass and plastic were among other types of containers investigated, but these were rejected for the more convenient, inexpensive gelatin capsule which could be discarded after being used.

Gelatin capsules were filled with a weighed amount of powder. When a mix was required a known volume of the liquid was

added with a syringe to a capsule before placing it in the amalgamator.

Mixing times of 5 to 10 seconds were investigated and although mixing was accomplished at 5 seconds in the greater majority of cases, a 7-second period was chosen in this series of tests. A change in tone of vibration is noted at the point mixing is completed. This occurred in approximately 4 to 5 seconds.

The powder-liquid ratio used was that found to produce a standard consistency disk diameter in accordance with American Dental Specification Number 9 for Dental Silicate Cement. One-fourth of the amount of powder and liquid used in determining the standard consistency ratio was used to mix the small specimen which would correspond approximately to the size used in clinical practice.

The speed of the Crescent Wig-l-Bug amalgamator used in this series of tests was measured with a Strobotac and found to be 3,200 vibrations per minute.

The torsion balance used in all powder weighings was sensitive to plus or minus 2.0 milligram.

A one milliliter tuberculin syringe was used for all measurements of the liquid.

The analytical balance used in the solubility and disintegration tests was sensitive to plus or minus 0.2 milligram.

2.2 Determination of Physical Properties

Tests were conducted in accordance with A.D.A. Specification No. 9 for Dental Silicate Cements. Results were obtained on both standard-sized specimens and on small specimens which would approximate the size used routinely in the dental office.

To overcome the problem of mechanically mixing the large amount of powder required for testing the large standard-sized specimens, the powder was divided into two equal parts. Each part was placed into a separate gelatin capsule, and the second capsule was mixed immediately after the first.

Several modifications in testing procedure were necessary in testing the small specimens.

The brass ring size used in testing cements for setting time was modified from the standard internal diameter of 9.5 millimeters to 6.9 millimeters for the small specimens. The size of the compressive strength specimen was reduced from 12 x 6 millimeters to 5.7 x 2.99 millimeters. The solubility and disintegration specimen was reduced to 25 percent of standard volume and the diameter was reduced from 20 to 15 millimeters (see Figures 1 and 2). The volume of cement used in the consistency test was reduced from 0.5 ml to 0.125 ml.

All tests were conducted in a controlled temperature room with a temperature range of 20-22°C and a relative humidity of 55-75%.

3. RESULTS AND DISCUSSION

3.1 Silicate Cements

The two phases investigated were: the effects of mechanically mixing the silicate cements at room temperature, and the effects when a coolant, such as ethyl chloride, was sprayed on the mixing container to chill the ingredients during the mixing procedure. The results are shown in Table 1.

The diameter of consistency test disks of the silicate cements decreased when mixed by mechanical means at room temperature, but a slight increase was noted when a coolant, such as ethyl chloride, was used to chill the ingredients during mixing.

The setting time of the mechanically mixed silicate cements with no coolant was reduced but the specimens cooled with an ethyl chloride spray during mechanical mixing were similar in setting time to those mixed with the spatula. All setting times were measured from start of mix. The setting time of a mechanically mixed silicate cement (standard-sized specimen) with no coolant exhibited a setting time of three minutes; whereas, the same cement mixed by the spatula showed a setting time of four minutes. It should be noted that only seven seconds are spent in mechanical mixing, while approximately one minute is spent in spatula mixing. Therefore the resulting working times between mixing and setting of the cement are approximately the same for both methods.

Little significant difference was noted in the compressive strengths of the specimens mixed at room temperature. A decrease was noted in small specimens of cement A and standard specimens of cement B when they were mixed by mechanical means and subjected to the ethyl chloride coolant spray.

The silicate cements with the exception of cement C exhibited an increase in solubility and disintegration when mixed by mechanical means with the large specimens (cement B) showing a somewhat smaller increase. The series of mechanically mixed specimens in which the powder to liquid ratio was adjusted to meet the consistency test disk diameter had approximately the same setting time and compressive strength as standard consistency spatula mixed specimens, but increased slightly in solubility.

The small test specimens of cement C gave unexpected results. When mixed mechanically with the coolant spray the consistency test disk decreased in comparison to those mixed by spatula with a corresponding slight increase in the compressive strength and a decrease in solubility. It was believed that this might be due to particle size, but a study of particle size showed this group to correspond closely in particle size to other cements used in this series of tests.

The high solubility noted in the small test specimens in part is due to the large 15 millimeter diameter of the test disk in relation to its small mass.

The large specimens mixed with the ethyl chloride coolant spray exhibited what was believed to be surface freezing and it is questionable as to what effect the ethyl chloride may have on the silicate cement, because undoubtedly some of the spray seeps into the mixing container. The smaller samples were more effectively mixed by mechanical means than the large samples with or without the aid of the coolant spray.

3.2 Zinc Oxide-Eugenol Cements

E. R. Squibb and Son zinc oxide U.S.P. and eugenol U.S.P. and S.S. White Z.O.E. brand zinc oxide and eugenol cement were used in all tests.

The sizes of the specimens were the same as for the silicate cements. The physical properties of large and small specimens when mixed by spatula and mechanical means are given in Table 2.

The physical properties of the zinc oxides apparently are affected to some extent when mixed by mechanical means as compared to spatula mixing, but the degree to which they are affected is not marked. A slight decrease is noted in the diameter of the consistency test disks of the mechanically mixed cements.

Little difference was noted in the setting times of the zinc oxides when mixed by the spatula or mechanical method. The heat generated in the mechanical mixing may account for the slight decrease in setting time found in most of the mechanically mixed specimens.

The compressive strength was higher for small specimens. The small specimens also showed a somewhat higher solubility and disintegration. This again may be due to the higher ratio of surface area to mass for the small solubility and disintegration specimens.

4. SUMMARY

4.1 Silicate Cements

1. Mechanical mixing of silicate cements using an amalgamator and gelatin capsule is a convenient and time-saving procedure.
2. Depending upon the particular brand and technic used the compressive strength may be decreased and the solubility and disintegration of a silicate cement may be either increased or decreased by mechanical mixing.

3. More detailed information on specific brands of cement and technics would be required before mechanical mixing of silicate cements could be recommended for clinical use.

4.2 Zinc Oxide-Eugenol Cements

1. The zinc oxide-eugenol cements show little difference in their physical properties when mixed by the spatula or by mechanical means.
2. Mechanically mixing the zinc oxide-eugenol cements offers a simple, rapid and more efficient method of mixing.

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Table 1. Properties of Silicate Cements Mixed by Spatula and by Mechanical Techniques

Property	Cement	Standard Size Specimens				Small Test Specimens		
		Spatula	Mech. Room	Mech. Room	Mech. Cooled	Spatula	Mech. Room	Mech. Cooled
Powder Liquid Ratio Gram per 0.4 ml	A B C	1.47	1.47	1.36	1.47	1.38 1.47 1.50	1.47	1.38 1.47 1.50
Consistency Diameter of Disk mm	A B C	25	17	25	28	22 23 19	22	25 25 16
Setting Time Minutes	A B C	4	3	3.75	4	4 4 3	2.5	3 4 3
Compressive Strength psi	A B C	27,600	27,000	26,700	21,700	16,400 17,200 25,300	17,000	12,300 17,900 26,400
Solubility and Disintegration %	A B C	0.47	0.55	0.66	0.56	0.49 0.81 1.01	1.20	0.70 1.13 0.70

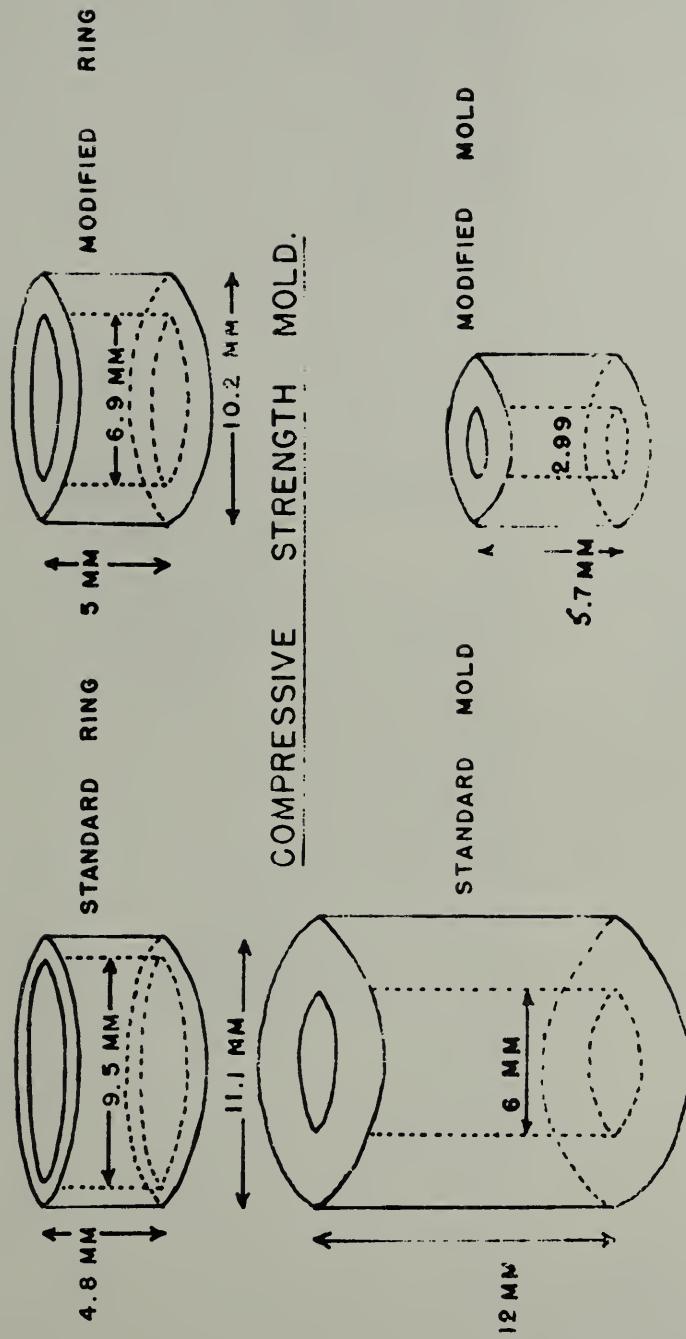
1 Powder-liquid ratio adjusted to produce consistency test
 disk 25 mm in diameter.

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Table 2. Properties of Zinc Oxide-Eugenol Cements
Mixed by Spatula and by Mechanical Techniques

Property	Cement	Large Test Specimens		Small Test Specimens	
		Spatula Mix	Mech. Mix	Spatula Mix	Mech. Mix
Consistency Diameter of Disk mm	ZnO (USP) Eug. (USP) S.S. White (Z.O.E.)	25	19	22½	15
Setting Time Minutes	ZnO (USP) Eug. (USP) S.S. White (Z.O.E.)	11 3/4	12½	11½	10½
Compressive Strength psi	ZnO (USP) Eug. (USP) S.S. White (Z.O.E.)	3,600	2,900	5,000	4,700
Solubility and Disintegration %	ZnO (USP) Eug. (USP) S.S. White (Z.O.E.)	0.029	0.10	0.065	0.10
		0.085	0.28	0.28	

SETTING TIME TEST RING.



COMPRESSIVE STRENGTH MOLD.



SOLUBILITY & DISINTEGRATION.

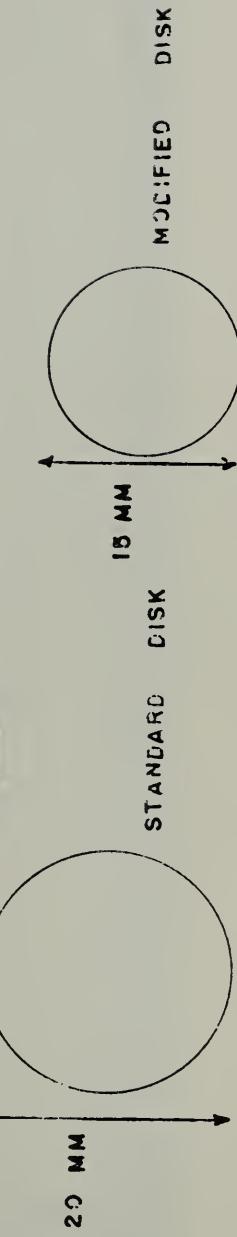


Figure 1. Comparison of dimensions of large and small specimens.

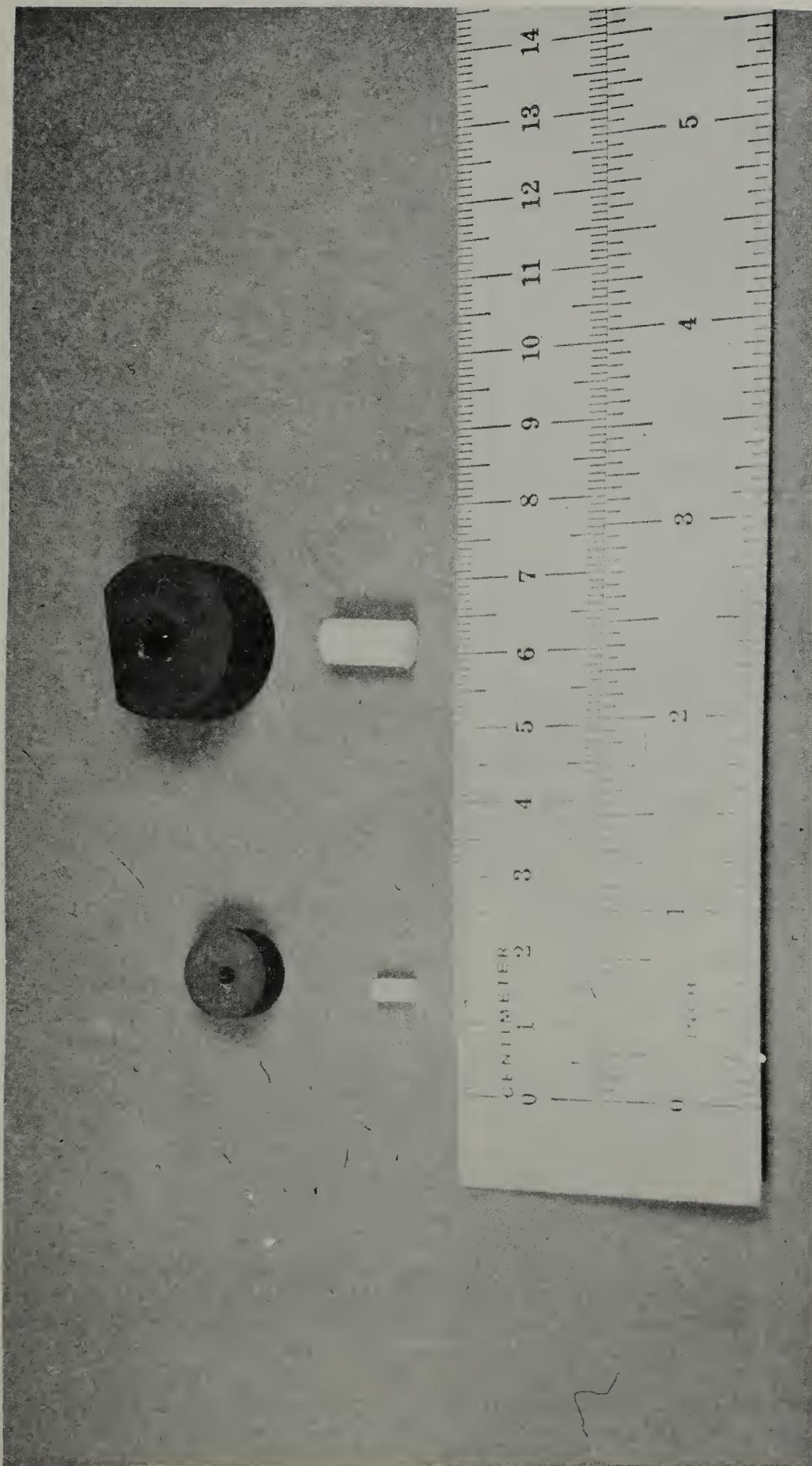


Figure 2. Comparison of small and large compressive strength specimens.

U. S. DEPARTMENT OF COMMERCE

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NATIONAL BUREAU OF STANDARDS

A. V. Astin, *Director*

THE NATIONAL BUREAU OF STANDARDS

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